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## Ion microprobe measurements of $^{18}\text{O}/^{16}\text{O}$ ratios of phosphate minerals in the Martian meteorites ALH84001 and Los Angeles

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**Abstract**—Oxygen isotope ratios of merrillite and chlorapatite in the Martian meteorites ALH84001 and Los Angeles have been measured by ion microprobe in multicollector mode.  $\delta^{18}\text{O}$  values of phosphate minerals measured *in situ* range from  $\sim 3$  to 6‰, and are similar to Martian meteorite whole-rock values, as well as the  $\delta^{18}\text{O}$  of igneous phosphate on Earth. These results suggest that the primary, abiotic, igneous phosphate reservoir on Mars is similar in oxygen isotopic composition to the basaltic phosphate reservoir on Earth. This is an important first step in the characterization of Martian phosphate reservoirs for the use of  $\delta^{18}\text{O}$  of phosphate minerals as a biomarker for life on Mars. Cumulative textural, major-element, and isotopic evidence presented here suggest a primary, igneous origin for the phosphates in Los Angeles and ALH84001; textural and chemical evidence suggests that phosphates in ALH84001 were subsequently shock-melted in a later event. Copyright © 2003 Elsevier Science Ltd

### 1. INTRODUCTION

The correlation between the chemical and isotopic compositions of the Martian atmosphere measured *in situ* by the Viking probes and trapped atmospheric components in shergottite impact glasses, is the basis for assigning a Martian origin to the SNC (Shergottite-Nakhilite-Chassigny) meteorites (Bogard and Johnson, 1983). While over twenty-five SNC meteorites are now recognized, only one sample (ALH84001) is older than 1.3 Ga. Merrillite ( $\text{Ca}_{18}(\text{Mg},\text{Fe})_2\text{Na}_2(\text{PO}_4)_{14}$ ) and apatite ( $\text{Ca}(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$ ) are important, albeit volumetrically minor, minerals in Martian meteorites, as they are the main carrier of rare earth elements (REE), and yield valuable information on D/H of Mars (Watson et al., 1994; Leshin et al., 1996). Rare earth elements in the Martian meteorites have been used to infer the petrologic history of these rocks, and of Mars as a whole (e.g., Wadhwa et al., 1994). Phosphate is also one of the most important chemical species for the existence of life on Earth. Phosphate plays several crucial roles in the cellular function and metabolism of all known organisms including conservation of energy in the form of ATP, and formation of key structural components of information storage molecules (i.e., DNA and RNA) and cell membranes (phospholipids). As a result, the reactions and distribution of phosphate in terrestrial systems are strongly influenced by biologic processes. The association of phosphate minerals (such as apatite) and carbonaceous matter enriched in  $^{12}\text{C}$  has been suggested to be chemical evidence for the oldest life on Earth ( $\sim 3.8$  Ga) (Mojzsis et al., 1996). Element ratios in phosphate minerals, as well as anomalous phosphorus concentrations of Martian soils, have been suggested as possible indicators of extinct life on Mars (Weckwerth and Schidlowski, 1995; Mojzsis and Arrhenius, 1998). It has recently been proposed that the oxygen

isotope ratio of phosphate ( $\delta^{18}\text{O}_p$ ) may be an important biomarker for both extinct and extant life in extraterrestrial systems, as well as a chemical indicator of hydrothermal activity (Blake et al., 2001). Hypotheses for possible evidence of life on Mars (McKay et al., 1996) and other extraterrestrial specimens need to be tested by every conceivable means. Application of  $\delta^{18}\text{O}_p$  values as a biomarker for life on Mars will require a clear distinction between biotic and abiotic  $\delta^{18}\text{O}_p$  signatures. An important first step in this approach is the determination of a baseline of unaltered  $\delta^{18}\text{O}_p$  values of important abiotic phosphate reservoirs on Mars so that biologically-produced  $\delta^{18}\text{O}_p$  anomalies can be detected. Currently, Martian meteorites are the only material available for determination of oxygen isotope signatures of phosphate minerals and reservoirs on Mars.

The ALH84001 meteorite is the only sample of ancient Martian crust known at the present time. A crystallization age of 4.5 Ga (Jagoutz et al., 1994; Nyquist et al., 1995) for the igneous minerals in this rock suggests that this meteorite holds clues to the earliest processes of crust formation on Mars. The high modal content of carbonate in this Martian meteorite ( $>1$  vol. %; Mittlefehldt, 1994) relative to others, coupled with a younger age for carbonate minerals (4.0 Ga; Borg et al., 1999) suggests that this meteorite provides our only window into a time when Mars may have had a warmer, and wetter climate. Putative evidence for biogenic activity in ALH84001 centers around the carbonate globules and minerals contained therein (McKay et al., 1996). Oxygen isotope ratios in ALH84001 carbonate and silica strongly suggest interaction between the crust and regolith/hydrosphere/atm systems on early Mars (Valley et al., 1997; Farquhar et al., 1998; Leshin et al., 1998; Eiler et al., 2002; Greenwood and McKeegan, 2002). Mass-independent sulfur isotope anomalies measured in individual pyrite grains in ALH84001 also indicate exchange between the crust and regolith/hydrosphere/atm system on early Mars (Greenwood et al., 2000a).

ALH84001 has undergone a complex petrogenetic history (e.g., Greenwood and McSween, 2001). It is currently believed

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that deposition of secondary carbonate and silica was bracketed by two shock events (Treiman, 1995; Greenwood and McSween, 2001). A shock age of 4.0 Ga (Ash et al., 1996) coupled with a similar age for carbonate (Borg et al., 1999), suggests that the second shock event was very old. Clearly, a third impact event was needed to liberate ALH84001 from Mars. Greenwood and McSween (2001) postulate that the phosphates (0.15% modally) are original late-stage igneous minerals, unrelated to secondary carbonate and silica deposition. Cooney et al. (1999) argue that phosphates and carbonates were shock-melted in ALH84001, although highly zoned oxygen isotope ratios in carbonate are difficult to reconcile with a shock origin (Warren, 1999). Eiler et al. (2002) offered a possible solution: ankeritic carbonates (which are unzoned in oxygen isotopes) formed by shock-melting of carbonate globules originally precipitated by aqueous solution.

Los Angeles is a younger basaltic shergottite meteorite, with trace carbonate believed to be terrestrial in origin (Rubin et al., 2000; Warren et al., 2003). Los Angeles comprises two stones which differ mainly in the proportion of late-stage crystallization features (Warren et al., 2003). A crystallization age of 170 Ma (Nyquist et al., 2000) puts Los Angeles in the range of other basaltic shergottites (Nyquist et al., 2001). Los Angeles has higher modal concentrations of chorapatite (0.9 and 1.0% for stones 1 and 2, respectively) and merrillite (1.5 and 1.7% for stones 1 and 2, respectively) than most Martian meteorites, which have <1% (except QUE94201 which has ~4% phosphate; Meyer, 1998). Mass-independent sulfur isotope compositions of sulfides in Los Angeles suggest that there was interaction between the crust and regolith/hydrosphere/atm systems on Mars (Greenwood et al., 2001); similar mass-independent sulfur anomalies have been found in other basaltic shergottites (Farquhar et al., 2000). Oxygen isotope ratios of mineral phases in Los Angeles have not previously been reported.

Despite the importance of phosphate minerals as carriers of trace and rare-earth elements and the potential of PO<sub>4</sub> as a biomarker for life on Mars, phosphates in Martian meteorites have not been studied extensively. Here we report the first measurements of oxygen isotope ratios of phosphate minerals in two Martian meteorites, ALH84001 and Los Angeles, using the UCLA ims 1270 ion microprobe in multicollector mode.

## 2. SAMPLES AND ANALYTICAL METHODS

Thin-sections of Los Angeles (UCLA 750) and ALH84001 (ALH84001.6) were examined using optical and electron microscopy to find suitable phosphate minerals for ion microprobe analysis. Backscattered electron (BSE) and secondary electron (SE) microscopy, as well as quantitative (WDS) analyses, were performed with the JEOL Superprobe at Yale University. Merrillite and apatite grains were located in the thin-sections of both meteorites. Operating conditions for electron microprobe analyses of phosphates were a 15 kV accelerating potential, 10 nA beam current, 10 s peak counting times and a 10 μm beam diameter. A defocused beam was used to avoid possible volatilization/migration in the beam diameter (Stormer et al., 1993; Greenwood and McSween, 2001). Augite in ALH84001 was also analyzed by electron microprobe. Operating conditions for augite analyses employed a 15 kV accelerating potential, 15 nA beam current and a focused electron beam. 20 s peak counting times were used for all elements analyzed except phosphorus, in which 120 s peak counting times were used. Appropriate mineral standards and matrix corrections were employed for all electron microprobe analyses.

*In situ* ion microprobe analyses of oxygen isotopes (<sup>16</sup>O and <sup>18</sup>O) in phosphate mineral grains were made with the UCLA ims 1270 ion

microprobe. The samples were sputtered using an ~1.8 nA Cs<sup>+</sup> primary beam focused to ~25 μm, with an impact energy of 20 keV. <sup>16</sup>O<sup>-</sup> and <sup>18</sup>O<sup>-</sup> secondary ions were collected simultaneously in Faraday cups and signals were amplified using Finnigan electrometers housed in a temperature-controlled evacuated chamber. A normal-incidence electron flood gun was used to neutralize positive charge buildup in the analysis area. Secondary ion beam intensities are given here in equivalent counts per second (cps). Count rates for <sup>16</sup>O<sup>-</sup> and <sup>18</sup>O<sup>-</sup> were typically 2 × 10<sup>9</sup> and 4 × 10<sup>6</sup> cps, respectively. Analyses consisted of 15 cycles of 10 s measurements; total analysis time, including a 2 min presputter time was under 5 min. Raw data were corrected for background and instrumental mass fractionation (IMF), defined as the fractional difference between the background-corrected raw <sup>18</sup>O<sup>-</sup>/<sup>16</sup>O<sup>-</sup> measured on a standard and its true <sup>18</sup>O/<sup>16</sup>O. Background measurements (n=26) were interspersed with sample (n=9) and standard measurements (n=41). Background measurements were made by conducting analyses with the Cs<sup>+</sup> source isolation valve closed, so that no primary ions can reach the sample. No drift was found in the interspersed background measurements; thus, the mean background intensity was subtracted from raw secondary ion beam intensities of the two masses of interest. The standard deviation of the background measurement on <sup>18</sup>O<sup>-</sup> was <10<sup>-4</sup> of sample and standard intensities, and therefore a negligible source of uncertainty. Correction for IMF was made using Bancroft, Ontario apatite and Tip Top Mine whitlockite as isotopic standards. Bancroft, Ontario apatite (δ<sup>18</sup>O = 10.48 ± 0.1‰) and Tip Top Mine whitlockite (δ<sup>18</sup>O = 15.85 ± 0.08‰) were measured by fluorination (Vennemann et al., 2002; T. Vennemann, pers. comm.). Ion microprobe measurements of δ<sup>18</sup>O of Bancroft, Ontario apatite ranged from 9.3 to 11.6‰ with a standard deviation of 0.63‰ (n=26). Ion microprobe measurements of the oxygen isotope composition of Tip Top Mine whitlockite gave δ<sup>18</sup>O ranging from 14.7 to 18.1‰ with a standard deviation of 1.21‰ (n=15). The small compositional difference between Tip Top Mine whitlockite and Martian merrillite suggests that whitlockite is an acceptable standard for correcting IMF during meteoritic merrillite oxygen isotope measurements by ion microprobe. The measured IMFs of whitlockite and apatite were -5.84 ± 0.12‰ and -4.65 ± 0.31‰, respectively, a difference of 1.19‰. Considering the large compositional difference between whitlockite and apatite, the small difference in IMF between these two phases suggests that measurement of oxygen isotopes of phosphate using the Cameca ims 1270 ion microprobe at these conditions should be relatively unaffected by minor compositional differences between the standard minerals and unknowns (e.g., Eiler et al., 1997). IMF is typically most strongly affected by major differences in the proportions of network-modifying cations (Eiler et al., 1997). The low energy secondary ions generated by the Cameca ims 1270 generally lead to much lower IMF than is typical of the high-energy secondary ions used by most other ion microprobes (e.g., Leshin et al., 1997; Greenwood et al., 2000b). The error assigned to an individual ion microprobe analysis reflects the reproducibility of the ion microprobe measurements of the standard mineral (external reproducibility) and cycle-to-cycle reproducibility (internal reproducibility) of the samples, but does not include uncertainties in the instrumental mass fractionation, the background correction, or the isotopic composition of the standard minerals as determined by conventional fluorination.

## 3. RESULTS

### 3.1. Petrography and Mineralogy

In Los Angeles, discrete, euhedral to subhedral grains of chlorapatite and merrillite are typically found adjacent to late-stage crystallization features in this meteorite, such as Fe-Ti oxides, pyrrhotite, K-,Si-rich glass, and material interpreted as pyroxferroite breakdown material (fayalite + silica + hedenbergite; Rubin et al., 2000 and Warren et al., 2003; see Xirouchakis et al., 2002 for an alternate interpretation), consistent with an igneous origin for these minerals (Fig. 1). Melt inclusions containing Fe-Ti oxides, pyrrhotite, baddeleyite, and K-, Si-rich melt are commonly found in the phosphate minerals in

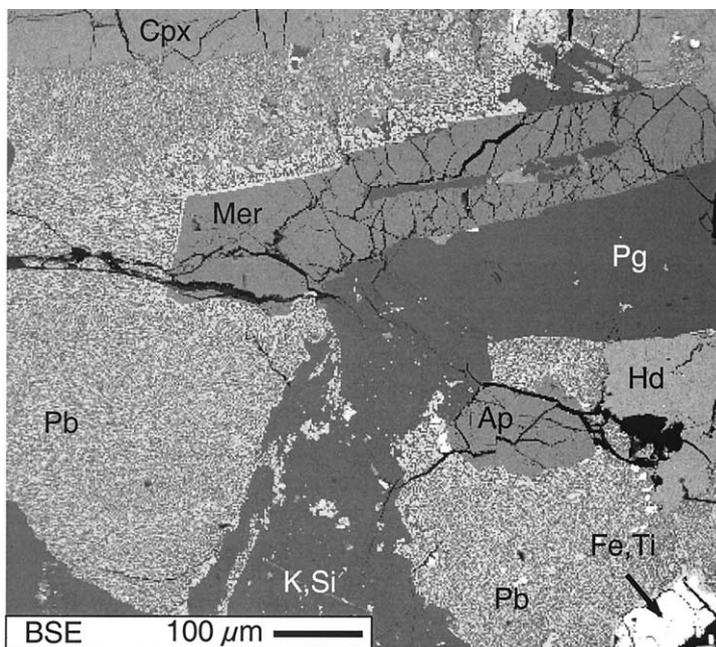


Fig. 1. Backscatter electron image (BSE) of Los Angeles. Subhedral chlorapatite (Ap) and euhedral merrillite (Mer) are part of a late-stage crystallization assemblage, which includes pyroxferroite breakdown product (Pb), an extreme iron-rich pyroxene that breaks down to the assemblage hedenbergite (Hd), fayalite, and silica (Lindsley et al., 1972). K-, Si-rich glass and Fe-Ti oxides are also closely associated with phosphates. Other phases shown are maskelynite (Pg) and augite (Cpx).

this meteorite. Chlorapatite grains have low fluorine concentrations (Table 1), a common feature of SNC meteorites (e.g., Stolper and McSween, 1979). Our analyses of phosphate minerals in Los Angeles are in excellent agreement with those of Warren et al. (2003) and Mikouchi (2001), but not Xirouchakis et al. (2002). Xirouchakis et al. (2002) did not identify merrillite or whitlockite in Los Angeles; they did identify apatite, but their published analyses suffer from low totals (~93%) and nonstoichiometry, suggesting that these analyses may be of poor quality.

The phosphate minerals in ALH84001 are very similar in major-element composition to those in Los Angeles (Table 1). The Mg/Fe ratio in merrillite is lower in ALH84001, consistent with the more Fe-rich composition of Los Angeles. Texturally, the phosphates in ALH84001 are in close association with plagioclase glass and/or carbonate, suggesting these three phases may share a related history. A region that we studied in ALH84001 is shown in Figures 2, 3, 4, and 5. The phosphate grain shown at the top of Figure 2 is intergrown with carbonate. In Figure 3 this same merrillite grain is shown at higher

Table 1. Electron microprobe analyses of apatite and merrillite in ALH84001 and Los Angeles.

	ALH gr1ap <sup>†</sup> (n = 5)	ALH gr3wh <sup>§</sup> (n = 3)	ALH gr4wh <sup>§</sup> (n = 8)	ALH gr5wh <sup>§</sup> (n = 6)	ALH gr6wh <sup>§</sup> (n = 4)	LA ap1 <sup>†</sup> (n = 5)	LA wh1 <sup>§</sup> (n = 5)	LA wh9 <sup>§</sup> (n = 5)
SiO <sub>2</sub>	0.18(11)	0.06(1)	0.07(2)	0.08(4)	0.04(2)	0.87(16)	0.09(3)	0.12(4)
FeO	0.16(5)	0.82(2)	0.81(8)	0.78(6)	0.71(11)	0.98(19)	4.73(6)	5.18(14)
MgO	0.13(15)	3.54(10)	3.58(9)	3.50(8)	3.53(6)	0.02(2)	1.03(7)	0.79(8)
CaO	53.9(4)	46.5(3)	46.4(2)	46.6(4)	46.6(2)	53.5(3)	46.9(2)	46.9(3)
SrO	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Na <sub>2</sub> O	0.31(5)	2.45(9)	2.46(11)	2.46(11)	2.38(3)	0.13(5)	1.21(7)	1.19(9)
P <sub>2</sub> O <sub>5</sub>	41.0(5)	46.2(10)	45.9(6)	46.4(7)	45.5(3)	40.5(8)	44.9(4)	44.9(6)
F	0.92(7)	b.d.	b.d.	b.d.	b.d.	1.13(44)	b.d.	b.d.
Cl	3.85(11)	b.d.	b.d.	b.d.	b.d.	2.25(55)	b.d.	b.d.
SO <sub>3</sub>	0.12(7)	b.d.	b.d.	b.d.	b.d.	0.15(7)	b.d.	b.d.
Total	100.57	99.57	99.22	99.82	98.76	99.53	98.86	99.08
O = F,Cl	1.26					0.98		
Total	99.31	99.57	99.22	99.82	98.76	98.55	98.86	99.08

Number in parentheses represents standard deviation in last significant figure(s).

b.d.: below detection limit.

<sup>†</sup> Apatite.

<sup>§</sup> Merrillite.

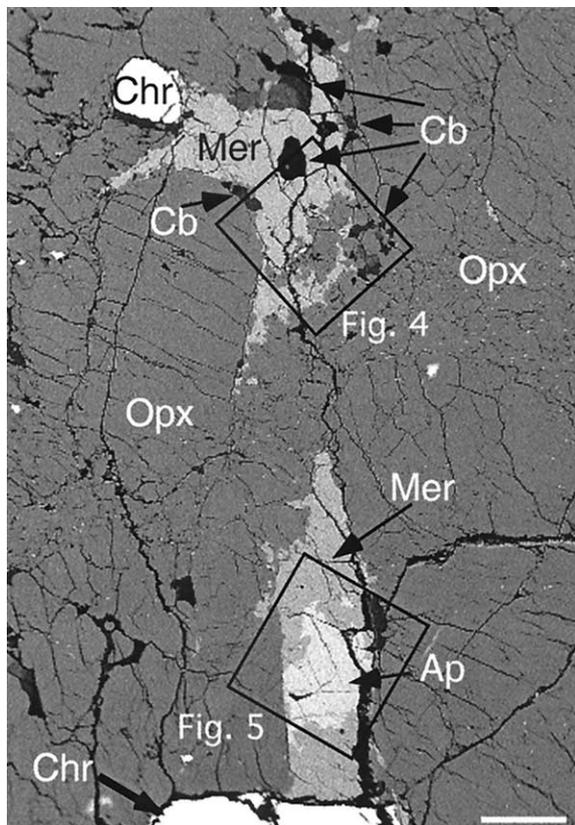


Fig. 2. BSE image of ALH84001 phosphate grains analyzed by ion microprobe. The merrillite (Mer) grain at the top of the image is in close association with carbonate (Cb) and chromite (Chr) and is shown in more detail in Figs. 3 and 4. The phosphate grain at the bottom of the image is an intergrowth of chlorapatite (Ap) and merrillite and is shown in more detail in Fig. 5 (boxes denote areas shown in Figs. 4 and 5). Orthopyroxene (Opx) is the dominant mineral in ALH84001. Scale bar is 100  $\mu\text{m}$ .

magnification. The large carbonate globule at the top of the image appears to have been disrupted and fractured. Merrillite and augite crosscut the center of the globule (Fig. 3). Figure 4 is a higher magnification view of the lower right portion of the merrillite grain shown in Figure 3. This large merrillite grain has a discontinuous rim of P-bearing augite at most orthopyroxene-merrillite grain boundaries. This can be seen best in the Ca and Mg K $\alpha$  X-ray images (Figs. 4c,d). A rounded grain of orthopyroxene can be seen within an augite rim (black arrow in Fig. 4d). Electron microprobe analyses of the discontinuous augite rim reveal resolvable P (Table 2). These analyses are not affected by secondary fluorescence; the analyses are  $\sim 5 \mu\text{m}$  from phosphate (location of electron microprobe analyses are shown in Fig. 4a). Analyses of orthopyroxene within 2  $\mu\text{m}$  of phosphate showed no resolvable P, under the same analytical conditions. Our ion microprobe spot can be seen in the BSE image (wh4, Fig. 4a). The edge of the ion microprobe spot is within 5  $\mu\text{m}$  of intergrown carbonate and augite. The ion microprobe spot is within 50  $\mu\text{m}$  of a large Mg-rich carbonate included within this merrillite grain.

The large merrillite-chlorapatite intergrowth shown in the lower part of Figure 2 is shown at higher magnification in Figure 5. The large ion microprobe pits seen in Figure 5 were

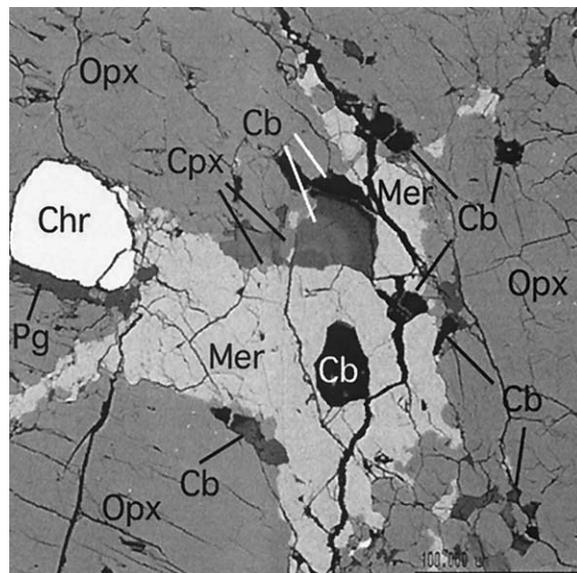


Fig. 3. BSE image of merrillite grain in ALH84001. Augite (Cpx) and merrillite (Mer) can be seen crosscutting the carbonate globule. Also shown are chromite (Chr), plagioclase glass (Pg), and orthopyroxene (Opx). The lower right portion of this grain is shown in more detail in Fig. 4. Scale bar is 100  $\mu\text{m}$ .

made in an earlier study (Boctor et al., 1998; N. Boctor, pers. comm.). Figure 5 shows the location of our ion microprobe spots in chlorapatite (ap1 and ap2) and merrillite (wh3). The chlorapatite is anhedral, and shows rounded contacts with the merrillite grain.

### 3.2. Oxygen Isotopic Compositions of Los Angeles and ALH84001 Phosphate Minerals

Results of ion microprobe analyses of oxygen isotopes in phosphates are given in Table 3. In Los Angeles, we measured oxygen isotopic compositions of one apatite grain (LAap3:  $\delta^{18}\text{O} = 5.4 \pm 0.6\text{‰}$  ( $1\sigma$ )) and two merrillite grains (LAwh7:  $\delta^{18}\text{O} = 5.9 \pm 1.2\text{‰}$  ( $1\sigma$ ); LAwh8:  $\delta^{18}\text{O} = 6.4 \pm 1.2\text{‰}$  ( $1\sigma$ )). These oxygen isotopic compositions are similar to a bulk-rock value for Los Angeles ( $\delta^{18}\text{O} = 4.53\text{‰}$ ; Rubin et al., 2000).

Similar oxygen isotopic compositions are found for phosphates in ALH84001. The merrillite grain (ALHwh4) intergrown with carbonate shown in Figure 3 has  $\delta^{18}\text{O} = 4.6 \pm 1.2\text{‰}$  ( $1\sigma$ ). Chlorapatite intergrown with merrillite (Fig. 4) has slightly lower  $\delta^{18}\text{O}$  values (ALHap1:  $\delta^{18}\text{O} = 4.0 \pm 0.6\text{‰}$  ( $1\delta$ ); ALHap2:  $\delta^{18}\text{O} = 2.8 \pm 0.6\text{‰}$  ( $1\delta$ )), but within error of the value for coexisting merrillite (ALHwh3:  $\delta^{18}\text{O} = 5.7 \pm 1.2\text{‰}$  ( $1\delta$ )). Two other merrillite grains had similar oxygen isotope ratios (ALHwh5:  $\delta^{18}\text{O} = 6.4 \pm 1.2\text{‰}$  ( $1\delta$ ); ALHwh6:  $\delta^{18}\text{O} = 5.7 \pm 1.2\text{‰}$  ( $1\delta$ )). The oxygen isotopic compositions of phosphates in ALH84001 are similar to those of mafic minerals in this meteorite (Clayton and Mayeda, 1996; Franchi et al., 1999).

## 4. DISCUSSION

### 4.1. Petrography and Mineralogy of Phosphates in Los Angeles and ALH84001

All Martian meteorites known to date contain chlorapatite and/or 'whitlockite' (e.g., McSween, 1994). The 'whitlockite'

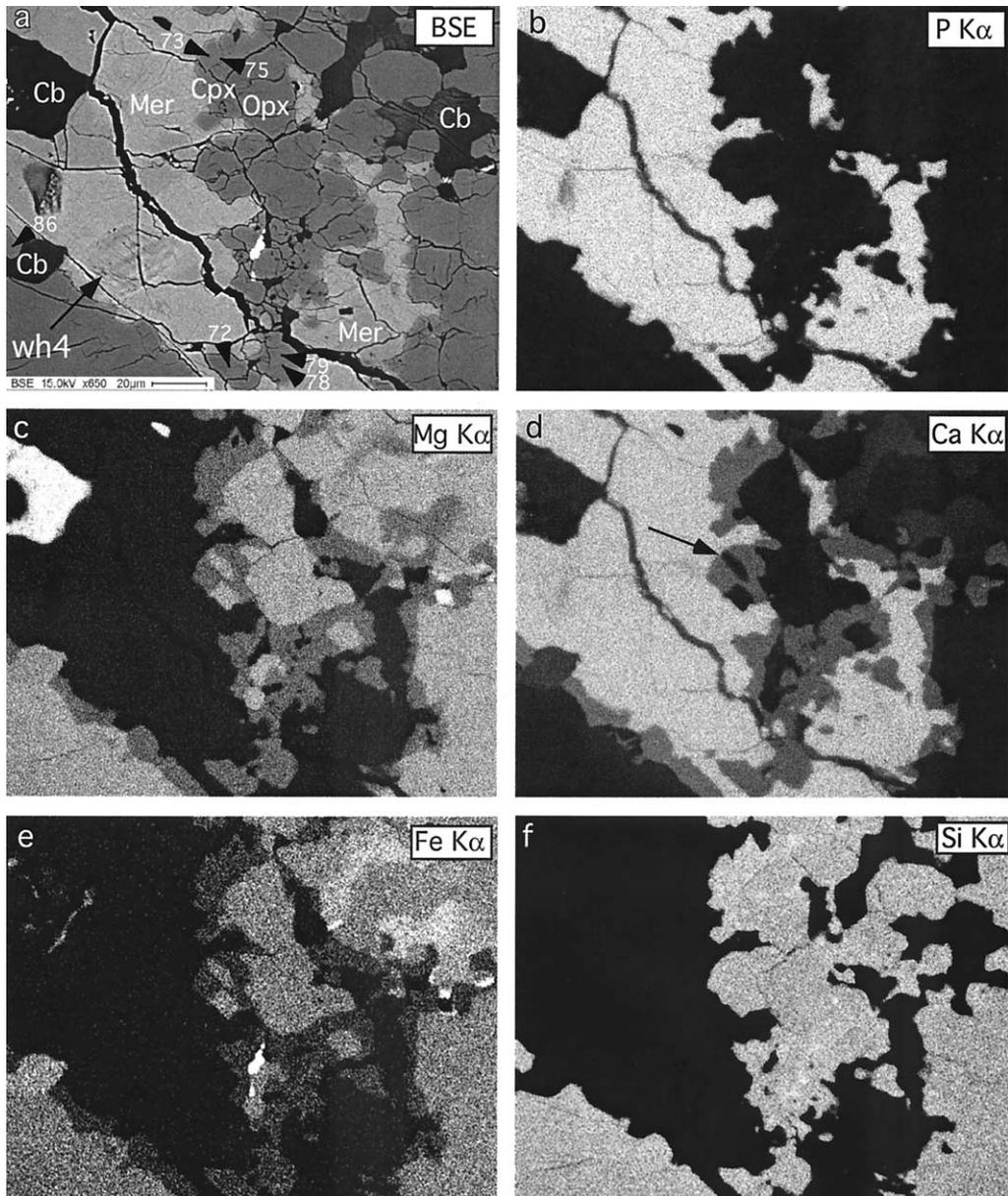


Fig. 4. (a) BSE image of merrillite (Mer) in ALH84001 shown in Figs. 2 and 3. Our ion microprobe spot (wh4) in this merrillite grain is shown. Also shown are electron microprobe analyses of augite reaction rim (numbers keyed to analyses in Table 2). Scale bar is 20  $\mu\text{m}$  and is valid for all of Fig. 4. (b) P  $K\alpha$  X-ray map, (c) Mg  $K\alpha$  X-ray map, (d) Ca  $K\alpha$  X-ray map, (e) Fe  $K\alpha$  X-ray map, and (f) Si  $K\alpha$  X-ray map show that augite forms a discontinuous rim at merrillite-orthopyroxene grain boundaries. A rounded orthopyroxene grain completely enclosed by augite is shown by the arrow in (d).

in Martian meteorites (and in fact most meteorites and lunar rocks) is actually merrillite. This misidentification is a result of the similar chemical compositions of merrillite and whitlockite. Merrillite has a slightly different structure than that of whitlockite (Prewitt and Rothbard, 1975; Dowty, 1977), is nominally anhydrous, and to date, is found only in meteorites (Rubin, 1997). Merrillite has been positively identified in ALH84001 (Cooney et al., 1999) and is likely to be the 'whitlockite' in all Martian meteorites. The nakhlites and Chassigny only contain one phosphate mineral, chlorapatite (Meyer, 1998).

The basaltic shergottite Los Angeles and the orthopyroxenite ALH84001 also contain merrillite and chlorapatite (Cooney et

al., 1999; Rubin et al., 2000). Phosphates in Martian meteorites are the main REE carriers (e.g., Wadhwa et al., 1994), and are the major repositories of deuterium and hydrogen as well (Leshin et al., 1996). REE systematics of phosphates in Martian meteorites are consistent with a magmatic origin (Wadhwa et al., 1994). Phosphates have generally been interpreted as late-crystallization features of Martian meteorites related to their igneous history (McSween, 1994), rather than as secondary features, although exceptions have been found (Gooding and Wentworth, 1991; Mojzsis and Arrhenius, 1998).

Phosphate minerals in the Los Angeles meteorite are euhedral to subhedral and associated with late-crystallization fea-

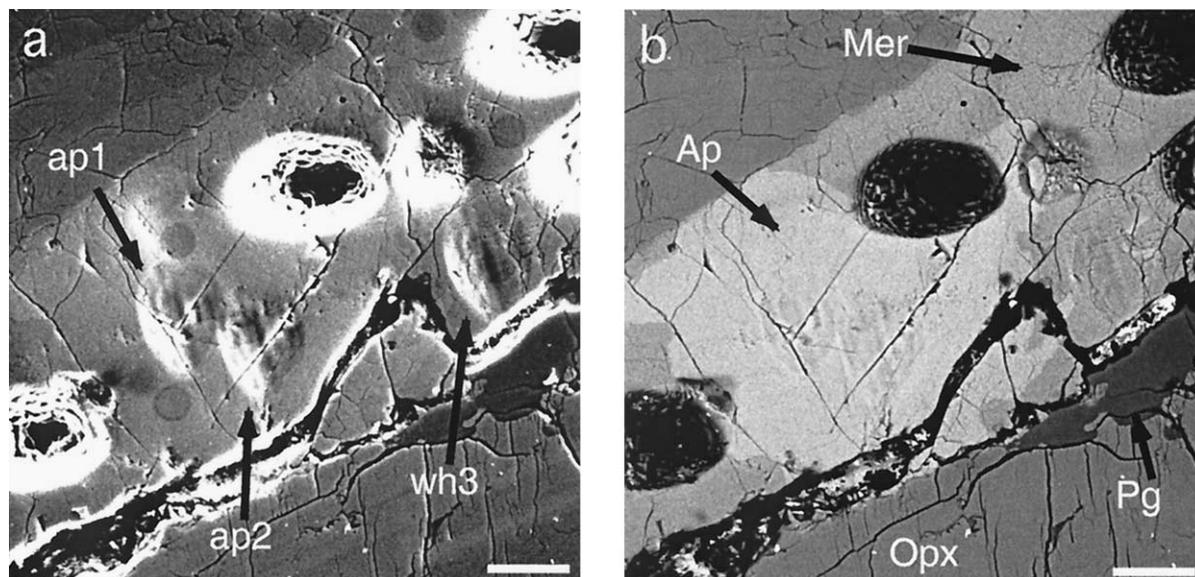


Fig. 5. (a) Secondary electron and (b) BSE image of chlorapatite and merrillite intergrowth shown in Fig. 2. Two ion microprobe spots in chlorapatite (ap1 and ap2) and one spot in merrillite (wh3) are shown. The other, large ion microprobe pits are not from this study. Plagioclase glass (Pg) and orthopyroxene (Opx) are also shown. Scale bars are 25  $\mu\text{m}$ .

tures, such as K-, Si-rich glass, Fe-Ti oxides, pyrrhotite, baddeleyite, and fayalite (Fig. 1). An occurrence of Cl-apatite crystallizing on the walls of a melt inclusion in a merrillite grain (Warren et al., 2003) suggests that merrillite crystallized first, and that apatite did not crystallize until higher volatile contents were reached through progressive crystallization (Sha, 2000), though this observation is at odds with the higher REE contents of merrillite in Martian meteorites which suggests that merrillite crystallizes after Cl-apatite. There is no petrographic evidence to suggest that phosphates in Los Angeles are not primary, late-stage igneous minerals.

Both merrillite and apatite were previously identified in ALH84001 (Berkley and Boynton, 1992; Mittlefehldt, 1994; Cooney et al., 1999). The textural association of phosphates and carbonates in this meteorite (Fig. 3) suggests that these two

minerals share a common history. Cooney et al. (1999) preferred an origin of shock melting of original igneous phosphates, which they argued was consistent with re-mobilization of phosphate near orthopyroxene that they observed. We observe a discontinuous, P-bearing augite rim at merrillite-orthopyroxene boundaries (Table 2, Fig. 4). The merrillite grain shown in Figures 2, 3, and 4 is intimately intergrown with carbonate. A carbonate globule at the top of the merrillite grain in Figure 3 is crosscut by augite and merrillite, suggesting that this occurrence of carbonate was not molten at the same time as the phosphate, and instead may have behaved in a brittle fashion. These observations suggest a high-temperature reaction of molten phosphate with solid orthopyroxene led to growth of P-bearing augite at merrillite-orthopyroxene boundaries.

Table 2. Representative electron microprobe analyses (wt.%) of augite in ALH84001. Locations of analyses are shown in Figure 4a.

	72	73	75	78	79	86
SiO <sub>2</sub>	52.74	52.80	52.92	52.64	52.42	52.24
TiO <sub>2</sub>	0.17	0.26	0.21	0.18	0.22	0.25
Al <sub>2</sub> O <sub>3</sub>	0.71	0.96	1.04	1.04	1.01	0.94
Cr <sub>2</sub> O <sub>3</sub>	0.27	0.37	0.46	0.52	0.45	0.42
FeO	8.22	8.27	7.97	8.10	8.16	8.69
MnO	0.25	0.26	0.31	0.25	0.31	0.32
MgO	15.25	15.19	15.28	15.24	15.18	15.36
CaO	21.19	20.68	20.65	20.18	20.88	20.12
Na <sub>2</sub> O	0.21	0.26	0.26	0.30	0.26	0.27
K <sub>2</sub> O	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
P <sub>2</sub> O <sub>5</sub> <sup>†</sup>	0.120 <sup>†</sup>	0.115 <sup>†</sup>	0.061 <sup>†</sup>	0.134 <sup>†</sup>	0.116 <sup>†</sup>	0.084 <sup>†</sup>
Total	99.13	99.17	99.16	98.58	99.01	98.69

Analytical conditions for elements besides phosphorus were 15 kV accelerating potential, 15 nA beam current, focused beam, and 10 s peak and background counting times.

Phosphorus analyses were undertaken at 15 kV accelerating potential, 20 nA beam current, focused beam, and 120 s peak and background counting times. 3 $\sigma$  detection limit for P<sub>2</sub>O<sub>5</sub> is 0.040 (wt. %).

b.d.: Below detection limit

Table 3. Analyses of apatite and merrillite in Martian meteorites ALH84001 and Los Angeles.

Sample	$\delta^{18}\text{O}\text{‰SMOW}^\dagger$	1 $\sigma$ error <sup>‡</sup>
<b>ALH84001</b>		
<i>Apatite</i>		
ALHap1*	4.0	0.6
ALHap2*	2.8	0.6
<i>Merrillite</i>		
ALHwh3	5.7	1.2
ALHwh4	4.6	1.2
ALHwh5	6.4	1.2
ALHwh6	5.7	1.2
<b>Los Angeles</b>		
<i>Apatite</i>		
LAap3	5.4	0.6
<i>Merrillite</i>		
LAW7	5.9	1.2
LAW8	6.4	1.2

<sup>†</sup>  $\delta^{18}\text{O} = \{[(^{18}\text{O}/^{16}\text{O})_{\text{sample}} / (^{18}\text{O}/^{16}\text{O})_{\text{standard}}] - 1\} \times 10^3$ , where the standard is Standard Mean Ocean Water (SMOW).

<sup>‡</sup> Error is due to counting statistics and includes uncertainty in the reproducibility of the standard minerals, but does not include uncertainties in instrumental mass bias or isotopic composition of standards.

\* Separate ion microprobe spots on same grain.

Cooney et al. (1999) state that merrillite and chlorapatite exhibit a replacement relation. We studied only one occurrence of chlorapatite in this meteorite, and are thus not prepared to make generalizations regarding the texture of all chlorapatite in ALH84001. We do not see evidence that the phosphate phases are in a replacement relationship.

Merrillite and apatite have similar solubilities in silicate melts and it has been suggested by Sha (2000) that the predominance of apatite over merrillite in terrestrial igneous rocks is due to higher volatile contents of terrestrial magmas relative to the Moon, Mars, and asteroidal parent bodies. Sha (2000) suggested that the occurrence of merrillite in the younger shergottites (~180 Ma; McSween, 1994) compared to the predominance of Cl-apatite in the older nakhlites (1.3 Ga; Nakamura et al., 1982) is consistent with Mars undergoing significant volatile depletion in the last 1 billion years. This idea is inconsistent with the evidence that ALH84001 has both merrillite and Cl-apatite. The hypothesis of Sha (2000) is also at odds with the high contents of Cl-apatite in the young basaltic shergottite Los Angeles (0.9–1.0 modal %) relative to merrillite (1.5–1.7 modal%) as well as high Cl-apatite modal abundances in other basaltic shergottites (Meyer, 1998). The modal proportions of these phosphate minerals would suggest that the parent magma(s) of the shergottites were not depleted in volatiles relative to the nakhlites. Martian magmas likely have lower volatile contents than terrestrial magmas due to their higher merrillite/apatite, but the phosphate mineral assemblages in the SNC's are inconsistent with the idea of Sha (2000) that the Martian mantle has suffered loss of volatiles through time.

#### 4.2. Oxygen Isotope Composition of Phosphates in Los Angeles and ALH84001

The  $\delta^{18}\text{O}$  values of merrillite and Cl-apatite in Los Angeles ( $\delta^{18}\text{O}$ : 5.4 to 6.4‰) are similar to the bulk rock value

( $\delta^{18}\text{O}$ =4.53‰; Rubin et al., 2000). This similarity is consistent with an igneous origin for the phosphates, though consideration of texture and trace element chemistry is necessary to ascribe an igneous paragenesis to these minerals. This suggests that basaltic phosphate on Mars is similar in oxygen isotopic composition to igneous phosphates on Earth, such as apatite derived from basaltic terranes ( $\delta^{18}\text{O}$ ~4 to 8‰; Mizota et al., 1992; Markel et al., 1994). This has important implications for the use of oxygen isotope ratios of phosphate as a biomarker for Mars sample return (Blake et al., 2001), and is discussed in detail in the next section.

The oxygen isotope ratios of merrillite and Cl-apatite in ALH84001 ( $\delta^{18}\text{O}$ : 2.8 to 6.4‰) are similar to the values for orthopyroxene in this meteorite ( $\delta^{18}\text{O}$  = 4.6‰; Valley et al., 1997) as well as the bulk rock value ( $\delta^{18}\text{O}$ : 4.64‰; Franchi et al., 1999;  $\delta^{18}\text{O}$ : 4.53‰; Clayton and Mayeda, 1996). Oxygen isotope ratios of olivine (Shearer et al., 1999) and plagioclase glass (Eiler et al., 2002) are also similar to orthopyroxene in ALH84001. Oxygen isotopic compositions of carbonate ( $\delta^{18}\text{O}$ : -10 to 25‰; Romanek et al., 1994; Valley et al., 1997; Leshin et al., 1998; Holland et al., 2001; Eiler et al., 2002) and silica ( $\delta^{18}\text{O}$ : 22 to 25‰; Greenwood and McKeegan, 2002) suggest that these phases are secondary, and not in equilibrium with phosphate minerals in this meteorite. Elevated  $\Delta^{17}\text{O}$  of carbonate also suggests a secondary origin for carbonate in ALH84001 (Farquhar et al., 1998).

The  $\delta^{18}\text{O}$  values of phosphates in ALH84001 are consistent with an igneous source for these minerals. An analysis of merrillite intergrown with Mg-rich carbonate (Figs. 2, 3, 4) suggests oxygen isotopic disequilibrium between merrillite and intergrown Mg-rich carbonate (Mg-rich carbonate  $\delta^{18}\text{O}$ : 20 to 25‰; Leshin et al., 1998). These isotopic compositions suggest that the high-temperature event that melted the phosphate and led to growth of augite rims at merrillite-orthopyroxene grain boundaries was short-lived, and did not lead to appreciable oxygen isotopic exchange between molten phosphate and carbonate. These observations are also consistent with the expected characteristics of a shock event.

#### 4.3. The Oxygen Isotope Ratio of Phosphate as a Biomarker

Oxygen isotope ratios of inorganic phosphates ( $\delta^{18}\text{O}_p$ ) occurring in soils, rocks or dissolved in natural fluids, that are anomalous or evolved from primary abiotic igneous source reservoir values, can be indicative of biologic activity (Blake et al., 2001). On Earth, due to the essential role of phosphorus to life processes and low concentrations of bio-available phosphate in most natural systems, biologic processes leave a strong imprint on the oxygen isotopic composition of phosphates (Kolodny et al., 1983; Luz and Kolodny, 1985; Blake et al., 1997, 1998, 2001). This is due largely to the strong temperature dependence of phosphate-water oxygen isotopic exchange and fractionation first demonstrated by the Longinelli and Nuti (1973) equation:  $T(^{\circ}\text{C}) = 111.4 - 4.3 (\delta^{18}\text{O}_p - \delta^{18}\text{O}_{\text{H}_2\text{O}})$ . The temperature dependence of phosphate-water oxygen isotope exchange results in marine biogenic phosphates, formed/processed at low temperature, with "heavy," positive  $\delta^{18}\text{O}_p$  values relative to non-biogenic phosphates formed at high temperature (i.e., igneous apatites). In the marine realm, the largest reservoir

of biologically-processed phosphate (e.g., dissolved phosphates, biogenic apatites, phosphorites) on Earth,  $\delta^{18}\text{O}_p$  values of recent phosphates are constrained by temperature and oxygen isotopic composition of seawater ( $\sim 0\%$ ) and range from  $\sim 20$  to  $25\%$  (Longinelli and Nuti, 1968; Longinelli et al., 1976; Shemesh et al., 1983; Lécuyer et al., 1996; Colman, 2002). These values are distinct from  $\delta^{18}\text{O}_p$  values of abiotic source phosphates, primarily igneous apatites, which range from  $\sim 4$  to  $8\%$  (Mizota et al., 1992; Markel et al., 1994).

Interpretation of  $\delta^{18}\text{O}_p$  values of phosphates in returned samples from Mars and other solar system bodies will require knowledge of the range of  $\delta^{18}\text{O}$  values characterizing various phosphate source and water reservoirs, and of the isotopic fractionations associated with processes that may potentially alter pristine  $\delta^{18}\text{O}_p$  values. To utilize  $\delta^{18}\text{O}_p$  as a biomarker for life on Mars, determination of the oxygen isotope ratios of Martian igneous phosphate is important, as igneous phosphate most likely represents original source phosphate that has not been chemically evolved by biologic or hydrothermal processes, and thus may serve as a baseline for interpretation of other phosphate occurrences. The present study is the first step in characterizing the Mars  $\delta^{18}\text{O}_p$  baseline.

Martian meteorites can be divided into three groups on the basis of age and lithology. ALH84001 is an ancient ( $>4.0$  Ga; Jagoutz et al., 1994; Nyquist et al., 1995; Ash et al., 1996) orthopyroxenite, the nakhlites (wehrlites/clinopyroxenites) and Chassigny (dunite) are  $\sim 1.3$  Ga (Nakamura et al., 1982) and the shergottites (basalts and lherzolites) are  $\sim 180$  Ma (Nyquist et al., 2001). The Martian meteorites possibly represent six phosphate reservoirs: 1) ALH84001, 2) nakhlites, 3) Chassigny, 4) basaltic shergottites, 5) lherzolithic shergottites, and 6) secondary phosphates (EETA79001). Here we have shown that the  $\delta^{18}\text{O}_p$  of an ancient Martian igneous phosphate reservoir (ALH84001) is similar to that of a much younger igneous phosphate reservoir (Los Angeles). The  $\delta^{18}\text{O}_p$  values of ALH84001 and Los Angeles are similar to  $\delta^{18}\text{O}_p$  values of terrestrial basalts ( $\sim 4$  to  $8\%$ ; Mizota et al., 1992; Markel et al., 1994). Of the other four potential phosphate reservoirs mentioned above, the nakhlites and Chassigny and the secondary phosphates in EETA79001 represent phosphate reservoirs that may not be similar to those measured in ALH84001 and Los Angeles. In the nakhlites, the correlation of  $\delta^{34}\text{S}$  of sulfide minerals and degree of subsolidus equilibration suggests that these rocks were exposed to fluids in the  $200$ – $400^\circ\text{C}$  range (Greenwood et al., 2000c). The small ( $<20$   $\mu\text{m}$ ) chlorapatite grains may have undergone oxygen isotopic exchange with these fluids in this temperature range. Hydrothermal fluids have the potential to modify oxygen isotope ratios of dissolved phosphate (Lécuyer et al., 1999; O'Neil et al., 2003). This suggests that phosphate in rocks like the nakhlites may have  $\delta^{18}\text{O}_p$  values unlike those of igneous phosphate, such as ALH84001 and Los Angeles. Low-temperature fluids which led to water-carbonate oxygen isotopic equilibration in the nakhlites (Farquhar and Thiemens, 2000) likely would not have modified  $\delta^{18}\text{O}_p$  of igneous phosphates.

The secondary phosphates in EETA79001 (Gooding and Wentworth, 1991; Mojzsis and Arrhenius, 1998) represent another potentially important phosphate reservoir on Mars. If these phosphates precipitated from low temperature, near surface fluids, the  $\delta^{18}\text{O}_p$  values would likely mirror the  $\delta^{18}\text{O}$  value

of the dissolved phosphate source (e.g., basaltic/igneous merrillite and apatite), unless there is an active biosphere on Mars. Due to sluggish  $\text{PO}_4\text{-H}_2\text{O}$  oxygen isotope exchange kinetics at low temperature ( $<70^\circ\text{C}$ ) dissolved inorganic phosphate does not undergo significant oxygen isotope exchange with ambient water in the absence of enzymatic catalysis (Tudge 1960; Longinelli et al., 1976; Kolodny et al., 1983; Lécuyer et al., 1999; O'Neil et al., 2003). Thus, at low temperatures, sedimentary phosphates would retain oxygen isotope ratios indicative of original source reservoir compositions if unaffected by biologically-mediated  $\text{PO}_4\text{-H}_2\text{O}$  exchange (Markel et al., 1994). Metabolism or enzymatic turnover of dissolved phosphate would lead to oxygen isotope exchange between phosphate and Martian fluids and evolution of secondary phosphate  $\delta^{18}\text{O}_p$  values away from igneous source values (Blake et al., 2001). Low-temperature secondary phosphate precipitation has been postulated to be an important process on Mars (Dreibus et al., 1996); characterization of this reservoir would be an important step in utilizing the  $\delta^{18}\text{O}_p$  biomarker for Mars sample return missions.

In summary, the  $\delta^{18}\text{O}_p$  biomarker can be a powerful tool for Mars sample return, provided that an accurate assessment is made of the oxygen isotope systematics of Martian phosphate reservoirs. This work has provided the first look at two Martian igneous phosphate reservoirs. Future work will include characterization of the other four phosphate reservoirs available for study in the Martian meteorites.

## 5. CONCLUSIONS

We have developed an *in situ* method for the analysis of oxygen isotope ratios of phosphate minerals using an ion microprobe in multicollector mode. This method allows for rapid analysis of small sample volumes in thin sections, and it is expected that this method will be useful for analysis of future returned samples from Mars and other solar system objects, as well as precious terrestrial samples.

Ion microprobe analysis of oxygen isotope ratios of phosphate minerals in the Martian meteorites ALH84001 and Los Angeles yield  $\delta^{18}\text{O}$  values of  $2.8$  to  $6.4\%$ . These values are similar to Martian meteorite whole-rock oxygen isotope ratios, suggesting an igneous origin for the phosphate minerals in these rocks. The  $\delta^{18}\text{O}$  values of Martian phosphate minerals are also similar to igneous phosphates and basaltic rocks on Earth (Taylor and Epstein, 1962; Markel et al., 1994). This is an important finding that further supports using the chemical evolution of elemental reservoirs and geochemical systems on Earth as an analog for Mars. Martian meteorites are the only materials available at present for the determination of oxygen isotope signatures of phosphate reservoirs on Mars. Cumulative textural, mineralogical and chemical evidence, including oxygen isotope ratios presented here, point to an igneous origin for the phosphate minerals in ALH84001 and Los Angeles. We have also presented evidence which suggests that phosphate minerals in ALH84001 were shock-melted after carbonate formation and underwent reaction at high-temperature with orthopyroxene to form augite at merrillite-orthopyroxene grain boundaries.

Igneous phosphate is a critically important reservoir to characterize isotopically as it represents original, source phosphate

that has not been chemically evolved by either biologic or hydrothermal processes, both of which have been suggested to have been important on Mars in the past. Thus, results presented here are an important first step toward development of phosphate oxygen isotope ratios as a biogeochemical indicator for exploration of Mars and other extraterrestrial systems. The analysis of phosphate oxygen isotope ratios by ion microprobe also opens up new opportunities for analysis of small and precious sample materials in other applications employing phosphate minerals.

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