MÖSSBAUER SPECTROSCOPY AND OXYGEN FUGACITY OF AMPHIBOLE-BEARING R-CHONDRITE LAP04840.

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Introduction: Oxygen fygacity is of paramount importance in constraining phase equilibria and crystallization processes of melts, as well as understanding the partitioning of elements between the core and silicate portions of terrestrial planets. Oxygen fugacity is typically studied using various indirect methods, including Fe-Ti oxide equilibria, olivine-pyroxene-spinel barometry, Eu oxybarometry, and $Fe^{3+}/\Sigma Fe$ by Mössbauer. In this study we bring all these methods to bear on the study of the amphibole-bearing chondrite LAP04840 (though the Eu results are as yet incomplete).

Sample Preparation: As described in [1], splits of powdered meteorite were made for whole rock spectra (by TES, FTIR reflectance, and Mössbauer). The remaining powders were hand-picked under a binocular microscope; we separated an olivine-rich fraction (8 mg) with minor opx, an amphibole-rich fraction (2 mg, with minor olivine and pyrrhotite), and a mica fraction (1 mg with minor olivine). Fortunately, the olivine doublets is easily distinguished in these spectra because of it high uadrupole splitting.

Analyses: Samples were analyzed on the electron microprobe at JSC as described in [2] for calculation of oxygen fugacity. Mössbauer analyses were made at Mount Holyoke College using a WEB model 302 spectrometer. Spectra were modelled using the Mex_Fieldd program, an implementation of software described in [3] and acquired from the University of Ghent courtesy of E. DeGrave. The program uses Lorentzian line shapes and solves full Hamiltonians for isomer shift and quadrupole splitting in each of two valence states. This routine produced better fits than quadrupole splitting distributions because of the highly overlapped nature of these spectra, which were largely mixtures of mineral rather than pure phases.

Mössbauer results: Results are presented in Table 1 for separates (Figure 1) as well as whole rock spectra (Figure 2). Parameters are extremely consistent from sample to sample, but the assignment of those doublets is made complicated by the fact that pyroxene, amphibole, and mica have very similar octahedral site geometries, and thus nearly indistinguishable Mössbauer parameters. XRD will be used to confirm the identities of the phases and constrain peak assignments.

The Fe^{3+} contents of the separates gives information to assess the oxygen fugacity under which the minerals equilibrated. The olivine + opx separate contains 5% of the total Fe as Fe^{3+} and only 6% of the total Fe as Fe^{2+} in opx. If the Fe^{3+} is only in the opx, then the mineral is roughly half Fe^{3+}; this would be highly unlikely based on all opx analyses in the literature. It appears more likely that the Fe^{3+} might be in the olivine; interestingly, the observed 5% would be analgous to what is observed in metasomatized, amphibole-bearing mantle xenoliths [4]. If the olivine is Fe^{3+}-bearing, it might be possible to observe humite-like interlayers or intergrowths of olivine with laihunite, magnesioferrite, magnetite, or even hematite at very fine scales with TEM, as has been done with oxidized terrestrial olivines; work is in progress to evaluate this possibility.

When the olivine and its Fe^{3+} are excluded from the amphibole spectrum, the remaining hornblende is 79% Fe^{3+}; this result is quite consistent with the 80% Fe^{3+} value obtained from EMP normalization. The mica is also Fe^{3+} rich, with ~65% of the total Fe as Fe^{3+} once the olivine and its related Fe^{3+} are factored out.

Table 1. Mössbauer Parameters for LAP04640,16

Sample	Mineral	I.S.	Q.S.	Area
Ol + Opx	Ol Fe^{2+}	1.18	2.96	53
	Ol Fe^{2+}	1.10	2.85	36
	Opx Fe^{2+}	1.13	2.08	6
	Ol? Fe^{3+}	0.28	0.40	5
Hb* + Ol	Ol Fe^{2+}	1.15	2.92	48
	Hb Fe^{2+}	1.04	2.59	5
	Hb Fe^{3+}	0.36	0.97	17
	Hb Fe^{3+}	0.20	0.35	11
Mica + Ol	Ol Fe^{2+}	1.19	2.89	31
	Mica Fe^{2+}	1.13	2.65	23
	Mica Fe^{3+}	0.30	1.23	15
	Mica Fe^{3+}	0.30	0.46	31
Whole Rock 45-125 um*	Ol Fe^{2+}	1.17	3.04	34
	Ol Fe^{2+}	1.15	2.81	32
	Opx or Hb Fe^{2+}	1.18	2.49	5
	Opx or Hb Fe^{2+}	1.14	2.06	7
	Fe^{3+}	0.46	0.65	9
Whole Rock <45 um*	Ol Fe^{2+}	1.17	3.06	25
	Ol Fe^{2+}	1.36	2.87	1
	Ol Fe^{2+}	1.14	2.83	45
	Opx or Hb Fe^{2+}	1.15	2.10	7
	Fe^{3+}	0.38	0.38	7

*Sample also contains pyrrhotite, with MS parameters of I.S. = 0.70 mm/s, Q.S. = 2.80 mm/s and B_{Hf} = 28.2 Tesla.

The whole rock spectra (Figure 2) of the two size fractions are nearly identical, though the <45 μm size fraction appears to have slightly more olivine (71%) than the 45-125 μm fraction (65%). As a result, the

former has slightly less Fe^{3+} (9%) than the latter (11%) because the olivine has the lowest Fe^{3+} content of the phases present.
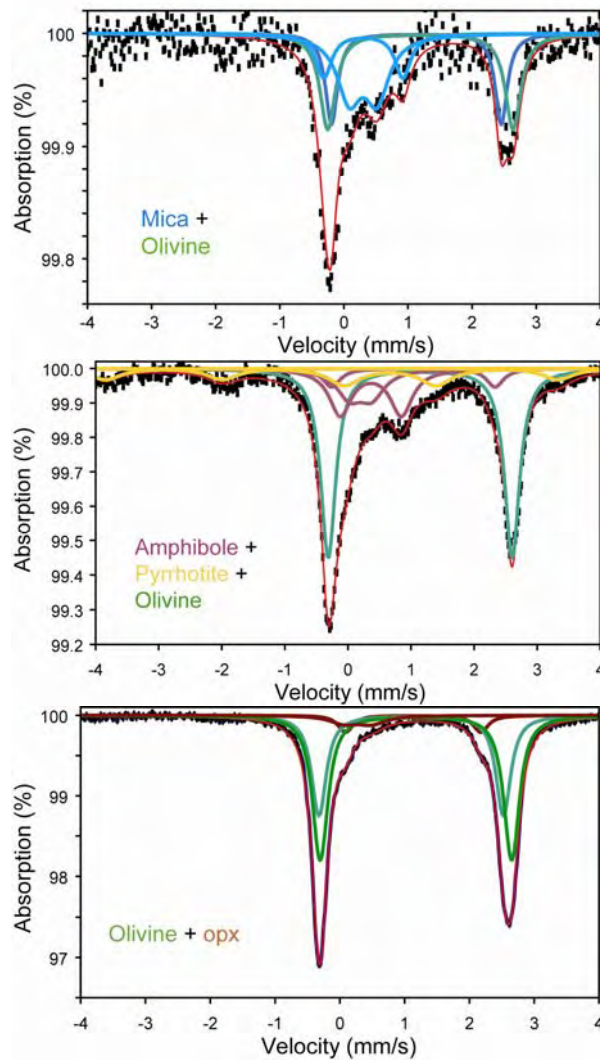

Figure 1. Mössbauer spectra of separates of mica (top), amphibole+pyrrhotite (middle) and olivine + opx (bottom). Doublets are labeled by color as indicated.

Results of Equilibria-based Calculations: We used the the QUILF calibration to calculate an oxygen fugacity from olivine-opx-spinel at 650°C, which is the temperature given by amphibole-plagioclase geothermometry [5]. With protest, the program gave QFM+0.75 +- 0.75 log units. This result agrees with qualitative estimates of QFM+0.5-1.0 for oxygen fugacity of metasomatized xenoliths with comparable Fe^{3+} contents [4].

Caveats and Conclusions: Of course, we recognize that the Fe^{3+} contents and oxygen fugacity recorded by these minerals may well be subject to resetting. The mineral assemblage is consistent with upper amphibolite facies conditions in terrestrial rocks, and these could certainly have oxidized the iron in the sam-

ple. Other mechanisms for alteration of Fe^{3+} include subsolidus re-equilibration and dehydrogenation of H-bearing minerals during shock from impact processes. However, the presence of hydrous phases requires water pressure for stabilization. Furthermore, the high Fe^{3+} contents observed here are consistent with the high oxidation states of the other R chondrites, as well as the absence of Fe metal.

It would be extremely useful to know the %Fe^{3+} contents that correspond to specific oxygen fugacities for each mineral. Work is in progress to experimentally quantify those relationships for olivine, pyroxene, amphibole, and mica (e.g. [6]), thus providing single mineral-based oxybarometers.
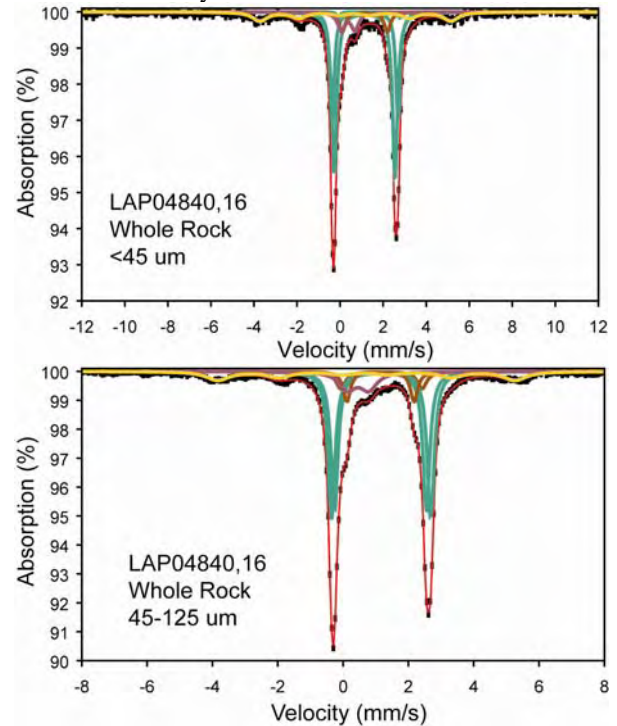

Figure 2. Mössbauer spectra of two different size fractions of the whole rock from LAP04840,16. Pyrrhotite is gold, olivine is green, and opx and amphibole are brown. Note the absence of peaks at, for example, -7.6 and 4.8 mm/s that would be characteristic of magnetite. Although magnetite and chromite were observed in thin section, they do not appear above detection limits in our Mössbauer spectra, perhaps because they are heterogeneously distributed throughout the sample. Efforts are underway to create a magnetite separate from a slightly different part of the chip to allow us to characterize the magnetite.

References: [1] Klima et al. (2007) *LPSC XXXVIII*, this volume. [2] McCanta et al. (2007) *LPSC XXXVIII*, this volume. [3] Wivel C. & Mørup, S. (1981) *J. Phys.*, *E14*, 605-610. [4] McGuire et al. (1991) *CMP*, 109, 252-264. [5] Treiman, A.H. et al. (2007) this volume. [6] McCanta et al. (2004) *Amer. Mineral.*, 89, 1685-1693.