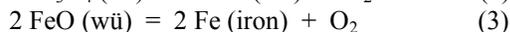
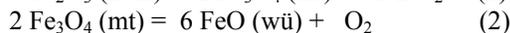
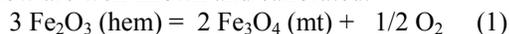


**MAGNETITE-MAGNESIOFERRITE PHASE RELATIONS AND APPLICATION TO ALH84001.** Andrea M. Koziol, Dept. of Geology, 300 College Park, University of Dayton, Dayton, OH 45469-2364 USA; (koziol@notes.udayton.edu).

**Introduction:** Oxygen fugacity ( $f_{O_2}$ ) is an important factor in planetary formation and evolution. Certain minerals or assemblages of minerals are stable only under certain  $f_{O_2}$  conditions (at a constant T and P) and can be recorders of ambient  $f_{O_2}$  during geologic processes. The best estimate of oxygen fugacity from mineral assemblages has implications, from large-scale models of planetary evolution to interpretation of single meteorites. For example, redox conditions are part of the discussion of the origin and history of shergottites, basaltic rocks in meteorites from Mars [1-4]. In addition oxygen fugacity may be an important factor to consider in the interpretation of the carbonate and magnetite assemblages seen in ALH84001 [5].

**Background:** *Oxygen fugacity.* For many planetary materials, the presence/coexistence of iron oxide minerals such as hematite (hem), magnetite (mt) and wü (wü) are used to estimate  $f_{O_2}$  at the time of formation. The P, T and  $f_{O_2}$  dependence for the equilibria below are well known and calibrated.



$\text{O}_2$  can be delivered to the minerals via a fluid or a mineral phase.

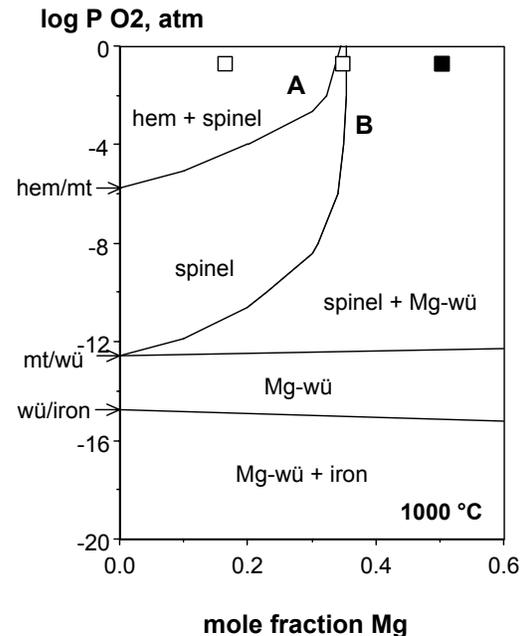
*On magnesioferrite.* Full consideration of  $f_{O_2}$  should consider magnesioferrite (mfer) ( $\text{MgFe}_2\text{O}_4$ ; Mg endmember of a solid solution of  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  with mt) and magnesiowüstite (Mg-wü) ( $\text{Fe, MgO}$  solid solutions). Addition of Mg will affect the activities of mt and wü in reactions (1) and (2) above. At a constant T and P, calculated  $f_{O_2}$  will be different than that of pure iron phases. Some workers have investigated this effect, either through experiments [6] or thermodynamic calculations [7-9].

**Analysis:** The petrologic and experimental literature has differing reports of the stability of  $\text{MgFe}_2\text{O}_4$  (mfer) versus  $\text{Fe}^{2+}\text{Fe}_2\text{O}_4$  (mt) plus MgO (periclase). The occurrence of mt + periclase versus mfer and how this depends on  $f_{O_2}$  is best explained by figure 1 below. This phase diagram is redrawn after a figure in [9] and based on data from [10].

At one bar and  $1000^\circ\text{C}$ , figure 1 indicates how the phase assemblage varies with Fe-Mg composition and oxygen partial pressure (essentially  $f_{O_2}$ ). The familiar iron oxide buffer reactions (reactions 1, 2, 3) are arrayed along the y-axis, at  $X_{\text{Mg}} = 0$ .

*Phase stability as a function of Fe-Mg composition.* As Mg is added to the system, it becomes part of a solid solution in mt (spinel) or wü. (As the mt phase varies in composition, it is referred to as spinel in the

diagram and in future discussions.) Mg cannot enter hem. Taking reaction (1) as an example, the  $f_{O_2}$



**Figure 1.** A plot of Fe-Mg composition (mole fraction Mg) versus  $\log P_{O_2}$ , at  $1000^\circ\text{C}$  and one bar total pressure (after [9]). Stable phase assemblage for each field noted. Spinel refers to (Mg, Fe)  $\text{Fe}_2\text{O}_4$  of variable composition. Mg-wü refers to magnesiowüstite. Positions of iron buffers noted along Y-axis. Hem/mt: reaction (1) mt/wü: reaction (2). Wü/iron: reaction (3) (see text). Squares: data from [11]. At  $X_{\text{Mg}} = 0.165$ : decarbonation product was hem + Mg-ferrite (open square). At  $X_{\text{Mg}} = 0.34$ : Mg-ferrite (open square). At  $X_{\text{Mg}} = .502$ : Mg-ferrite + MgO (filled square). Note; how this diagram changes with temperature is unknown.

in equilibrium with Mg-bearing mt increases (is less negative) than with the pure  $\text{Fe}^{2+}$  system. Note that this effect is not linear. Consider a range of oxide compositions at constant oxygen pressure. At atmospheric composition ( $\log P_{O_2} = -0.7$ ) hem and mfer are stable at low Mg mole fractions, mfer and a (Mg, Fe)O phase at high Mg mole fraction, and there is a small range of composition where mfer alone is stable.

*Phase stability as a function of  $f_{O_2}$ .* Consider one composition that, at constant temperature, experiences different  $\text{O}_2$  partial pressures (essentially different  $f_{O_2}$ ). At a bulk composition of  $X_{\text{Mg}} = 0.1$ , the assemblage hem + mfer, if equilibrated at a more negative (more

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reducing)  $f_{O_2}$  below curve A, should react to form a magnesioferrite spinel with a formula of  $(Mg^{2+}, Fe^{2+})(Fe^{3+})_2O_4$ . At even more negative  $f_{O_2}$  (below curve B) mt ( $Fe_3O_4$ ) and Mg-wü are stable. Previous work does not address whether composition of phases varies with changes in bulk composition, or whether the proportion of phases (i.e. more mt at high Fe content) varies. [9] suggest that above  $\log P_{O_2}$  of  $-10$  the wü phase should be almost pure MgO. Below this value, they suggest that wü becomes more Fe-rich.

**Previous studies:** There is support however for the general form or topology of this composition- $O_2$  pressure diagram. The data of [11] (squares) are plotted at  $\log P_{O_2} = -0.7$  (atmospheric  $P_{O_2}$ ) and confirm the essential shape of this diagram. They oxidized siderite ( $FeCO_3$ ) – magnesite ( $MgCO_3$ ) carbonate solid solutions in air and noted that hem + mfer formed at a composition of  $X_{Mg} = 0.164$ ; mfer formed at  $X_{Mg} = 0.348$ , and mfer and MgO formed at  $X_{Mg} = 0.502$ . Other siderite-magnesite decarbonation studies performed in atmosphere result in these assemblages also [6, 12-15]. There are a number of intriguing studies where siderite-magnesite carbonate solid solutions were heated with  $f_{O_2}$  less than atmospheric  $f_{O_2}$ , though the actual value was not defined or reported, nor were phase compositions listed. A magnesiowüstite phase and a very iron-rich spinel phase were reported [16-19].

**Application:** *Carbonate and magnetite assemblages in ALH84001.* The ALH84001 meteorite is a coarse-grained orthopyroxene [20, 21] containing magnesite-siderite carbonate globules. Scientists have discovered suggestive but not conclusive evidence of former life [20] in this meteorite. Small magnetite grains occur both in the core and rim of these globules. The presence of these pure nanophase magnetite grains is considered one of several lines of evidence supporting the hypothesis of former life on Mars [22-24]. The argument is made that magnesioferrite would form by inorganic decarbonation of magnesium-bearing siderite. But magnetite is the phase that is seen in the carbonate globules, as described above.

Recently, detailed intense study of the carbonate parageneses in ALH84001 revealed one micron sized patches of fine-grained periclase (MgO) associated with tiny voids in Mg-rich carbonate [25], or Ca-bearing brucite (MgOH), which may be a hydration product of Ca-bearing periclase [26]. An inorganic origin for the magnetite spinel with periclase makes sense if bulk composition and  $f_{O_2}$  during formation were in the spinel + Mg-wü field of figure 1. For the ALH84001 meteorite, the magnetite is the spinel phase and periclase (MgO) is the magnesiowüstite phase.

It is perilous to apply equilibrium phase diagrams to a rock that has clearly experienced non-equilibrium

processes. Figure 1 applies outlines parageneses at  $1000^\circ C$  only. However such an analysis can provide a rough sense of relative  $f_{O_2}$  if the magnetite grains in ALH84001 formed inorganically.

In Fig. 1, line B is the composition of spinel in equilibrium with Mg-wü. A spinel of nearly pure iron composition (i.e. mt) in equilibrium with Mg-wü (perhaps pure periclase in composition) would be stable at low  $f_{O_2}$  of  $\approx -12$ , near the mt/wü buffer. Further experimental work would clarify these phase relations.

**Conclusions:** It is possible to form mt from Fe-Mg carbonate under certain conditions. For ALH84001, formation of magnetite with or without MgO via decarbonation reactions would require low  $f_{O_2}$  (near mt-wü).

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