Paradoxes and perceptions in color identification of paleo-redox conditions in peletic rocks

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Abstract

Identification of initial sedimentary redox conditions by color in peletic rocks can be potentially misleading. Conventionally, black indicates anoxic conditions; green: slightly anoxic, and red: oxic. Mineral stability fields of common Fe and Mn sedimentary minerals, as depicted in Eh-Ph diagrams for 0, 25, 100, and 200 degrees Celsius, shows that not all black rocks are anoxic nor red rocks oxic. We recommend that estimations of redox conditions should be based on further mineralogical, chemical and/or paleontological evidence and color used only as a descriptor of the color of the rock.
Keywords: redox, color, Fe, Mn, shales, Eh-pH

Introduction

C. V. Guidotti was interested in all aspects of peletic rocks not only those of the metamorphic grade. He approached us in the late '90's knowing we had been working on redox conditions in Phanerozoic rocks, generally sediments and low rank shales, to work jointly on investigation of geochemical conditions in peletic rocks throughout various metamorphic grades. Charley learned to use Eh-Ph diagrams as a graduate student from Bob Garrels' mythical geochemistry class (Guidotti, p 98,102, in Schmitt, 1962).Wilde, Quinby-Hunt, and Guidotti (1997) presented an abstract outlining some of the paradoxes in the Eh-Ph diagrams of the Fe system using increasing temperature as a proxy for metamorphic rank.   Sadly we never pursued this further into other systems and into a more formal paper. The following is our attempt to remedy this omission for early diagenetic temperatures; although without Charley's most valued insights.

Background

There is a long held perception that in lieu of other information, the color of many peletic rocks in the field gives an indication of relative redox conditions. Briefly stated that red rocks indicated 'oxic'; green: 'slightly reduced'; and black: highly reduced. Even in classic anoxic 'black' shales such as those of the Ordovician of New York (Berry, 1962), the field descriptions show variations in color including green and red which seemingly belie anoxic conditions. To examine these potential paradoxes we follow Baas-Becking and others (1960), Krumbein and Garrels (1952), and Garrels and Christ (1965) in the use of Eh-pH diagrams for the interpretation of natural systems. and demonstrate for common and potentially pigmenting Fe and Mn mineral phases that this is not universally true and in many cases very misleading. We use the Fe and Mn composition of the Small Falls Formation (Cullers and others, 1997) as an example in

honor of Charley's long romance with the metamorphic rocks of Maine. Van Baalen (this volume) gives a progress report on their joint work on the Small Falls, citing potential variation in anoxia through whole-rock chemical analyses.

Iron System

Figure 1 depicts the Eh-Ph diagrams of the mineral stability in the Fe-S-O system for hematite (Fe_2O_3), pyrite (FeS_2), pyrrhotite ($Fe_{.87}S$), magnetite (Fe_3O_4) at temperatures of 0, 25, 100, 200 degrees Celsius. Concentrations were Fe = $4e^{-4}$ M Small Falls (Cullers and others, 1997) and S = 2 e^{-3} M (Berner, 2004, p. 446). As shown hematite, a strong red pigment, has an appreciable stability range in the anoxic field below an Eh of 0. Accordingly if hematite were introduced into sediments, at these temperatures, they potentially would be colored red even if the interstitial conditions were anoxic. We stress the hematite does not have to form in anoxic conditions, just that it would be stable and survive early diagenesis. However, oxidants such as nitrate and nitrate, could produce authogenic hematite below Eh 0, if present in sufficient quantities (Stumm and Morgan (1970, p. 334). Nitrate and nitrite are likely to be common in the upper pycnocline in the pre Devonian world, with lower atmospheric oxygen before the development of land plants (Wilde, 1987, Canfield, 1998). In the modern ocean nitrate, and nitrite are found in limited but in sufficient amounts in the oxygen minimum zones (Anderson and others, 1982). Additionally, Konhauser and others (2002) suggested that the banded iron formations may have been produced by phototrophic bacteria in the low oxygen world of the Precambrian. Introduction of hematite into anoxic waters, for example, as in lateritic sediments, would not be an uncommon occurrence in tropical areas, particularly in near shore areas where organic productivity would deplete oxygen in the overlying water column. Darwin (1860, p. 5-6) noted the occurrence red dust on the Cape Verde Islands extending to South American apparently blowing across the Atlantic during the Harmartan season in the Sahara. Thus red pigment could be introduced into the hemi-pelagic component of marine sediments. In summary, if present, hematite may color sediment red in the following anoxic conditions.

<div align="center">Eh value at lower Hematite Boundary for pH 7</div>

0   C   with FeS_2…………..   -0.1

25 C   with FeS_2………….   -0.2

100 C   with FeS_2 …………   -0.3   and Fe_3O_4
200 C   with Fe3O4………..   -0.4

For more acidic conditions than pH 7, hematite is less stable in anoxic conditions.

<div align="center">Minimum pH for hematite stability at redox boundary (Eh =0)</div>

0   C   with FeS_2…………..   5.5

25 C   with FeS_2………….   4.8

100 C   with FeS_2 …………   3.6

200 C   with Fe_3O_4………..   2.8

For more alkaline conditions, hematite is more stable in more anoxic conditions.

Minimum Eh (maximum anoxicity) for hematite stability within stability field of water

0   C   with Fe_3O_4..........   -0.4 at pH 14

25 C   with Fe_3O_4..........   -0.6 at pH 14

100 C   with Fe_3O_4 ....   -0.82 at pH 14

200 C   with Fe_3O_4..........   -1.3 at pH 14

Within the stability field of water and these typical Fe concentrations, anoxic sediments could be red (hematite), green (fine grained pyrite?), or black (magnetite).

Manganese System

Figure 2 shows the Eh-Ph diagrams for the mineral stability in the Mn-S-O system for, pyrolusite (MnO_2), manganite (Mn_2O_3), hausmanite (Mn3O4), alabandite (MnS). In all cases over natural Eh-Ph conditions, these minerals would color a sediment black. Thus, the black color of any sediment with significant amounts of Mn minerals can not indicate uniquely redox conditions.

Redox Indicators

If color is a potentially ambiguous redox indicator, what can one use?? Jones and Manning (1994) have proposed eight redox indicies: DOP (degree of pyritisation: (Berner, 1970), C/S, U/Th, authogenic U, V/Cr, Ni/Co, Ni/V, (Cu+Mo)/Zn, based on Jurassic rocks.   Berner and Raiswell (1983) suggested significant organic carbon content would be a sufficient anoxic indicator. Certainly graphite would be an anoxic indicator for metamorphic rocks such as observed in the Small Falls (Cullers and others, 1997, Van Baalen, this volume). Quinby-Hunt and Wilde (1994) proposed four chemical zones for 'black rocks' using ranges of Fe, Mn, and V. Wilde and others (1996) used the Ce anomaly to identify relative redox conditions, although without assigning Eh, pE, or PO_2 values. Basically, these are still qualitative indicators, with no confirmed relation of the various ratios to actual Eh or pH values. Another perplexing problem is the confusion of whether the assigned redox conditions refer to the sediment or the overlying waters. In general, low porosity-low permeability sediments such as muds would be anoxic (below Eh = 0) at or just below the sediment surface regardless of the redox potential of the overlying waters.

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Figures
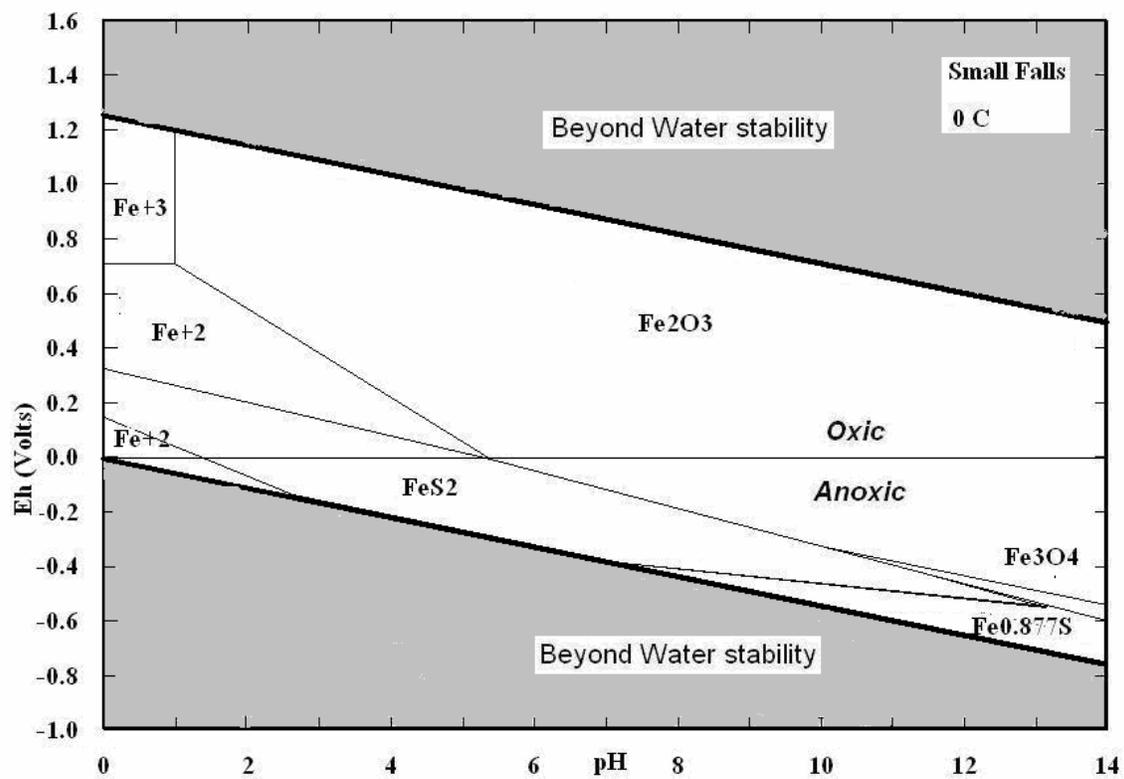
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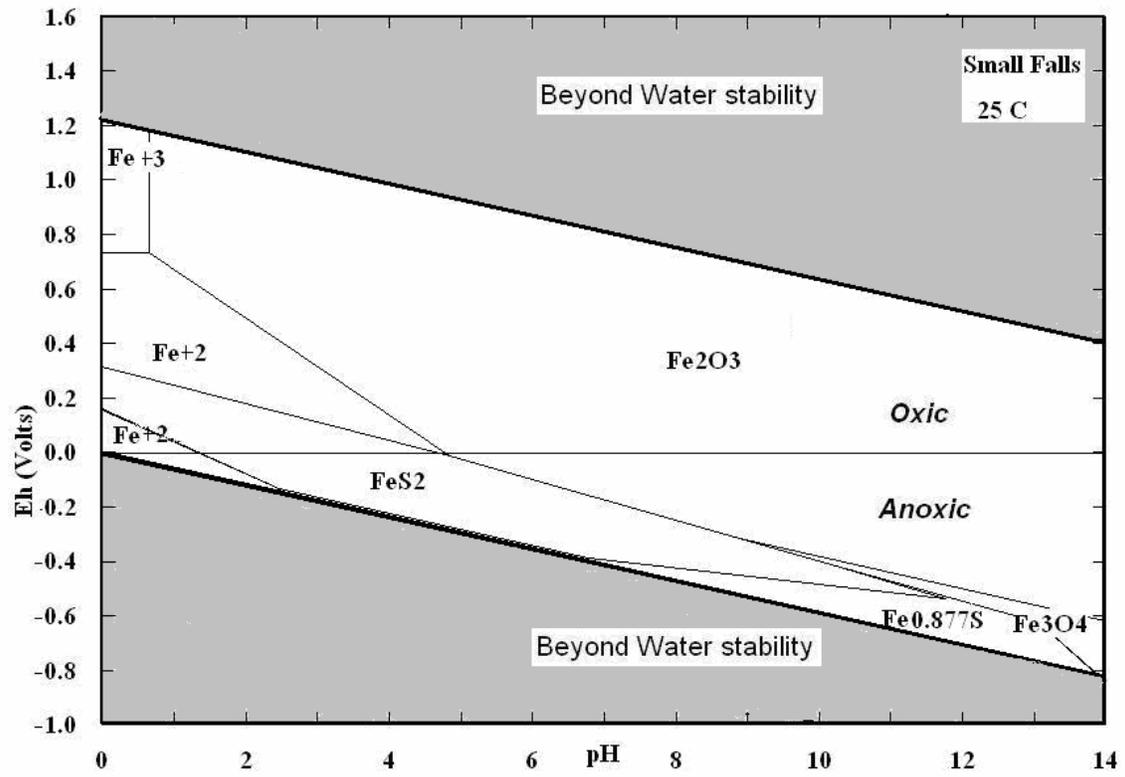
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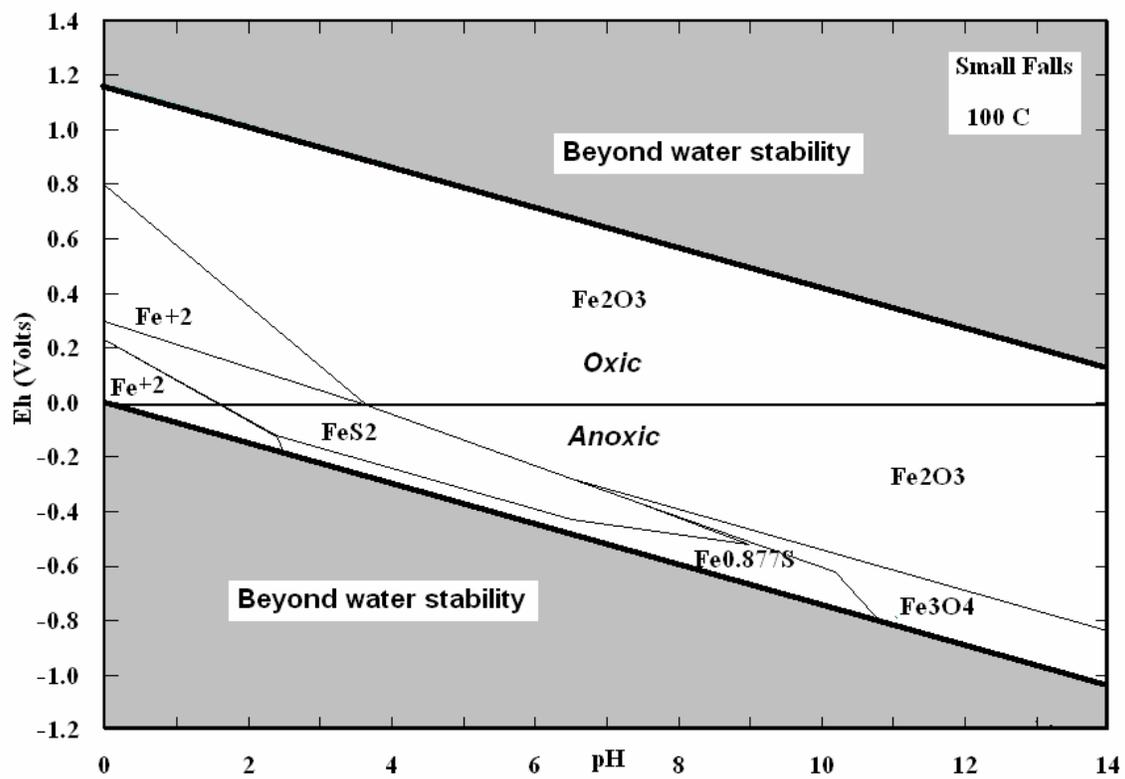
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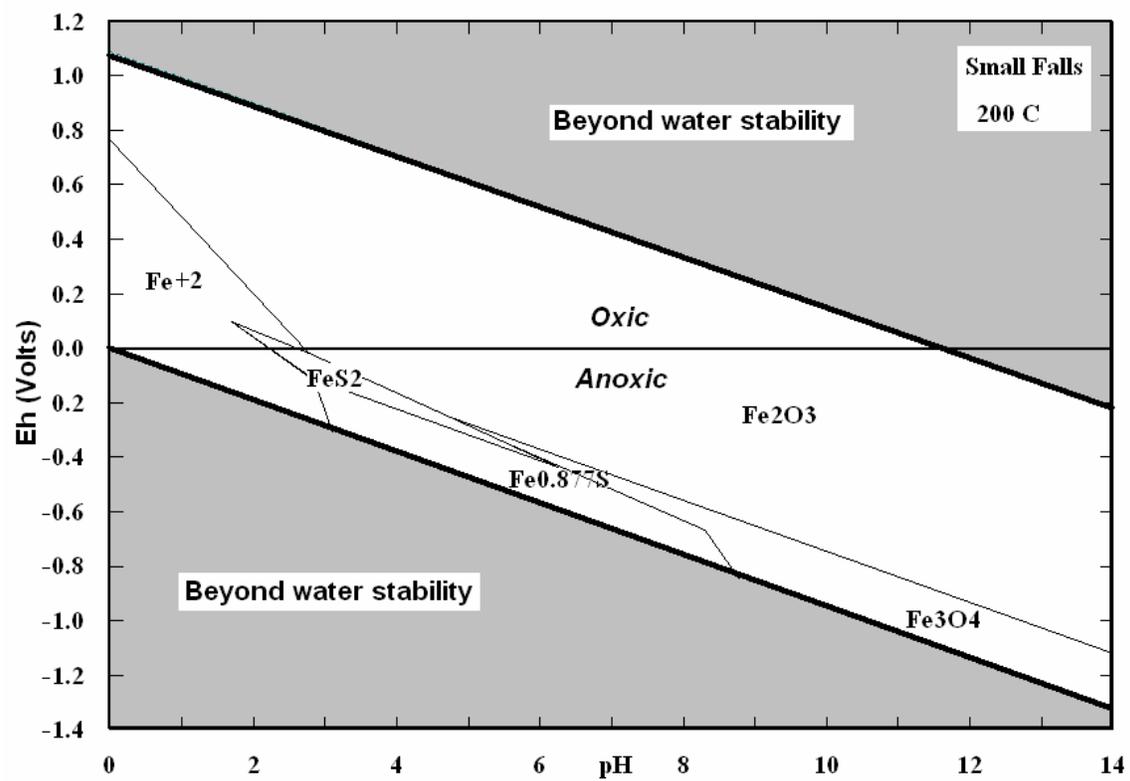
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Figure 1. Eh-pH diagrams for Small Falls concentration Fe ($4e^{-4}$ M) - Silurian sea water S ($2e^{-3}$ M). A: 0 degrees C, B: 25 degrees C, C: 100 degrees C and D: 200 degrees C.

A

B

Small Falls 100 C

Beyond water stability

Mn+2

MnO2

Mn2O3

Oxic

Anoxic

Mn+2

Mn3O4

MnS

Mn(OH)2

Beyond water stability

Eh (Volts)

pH

0   2   4   6   8   10   12   14
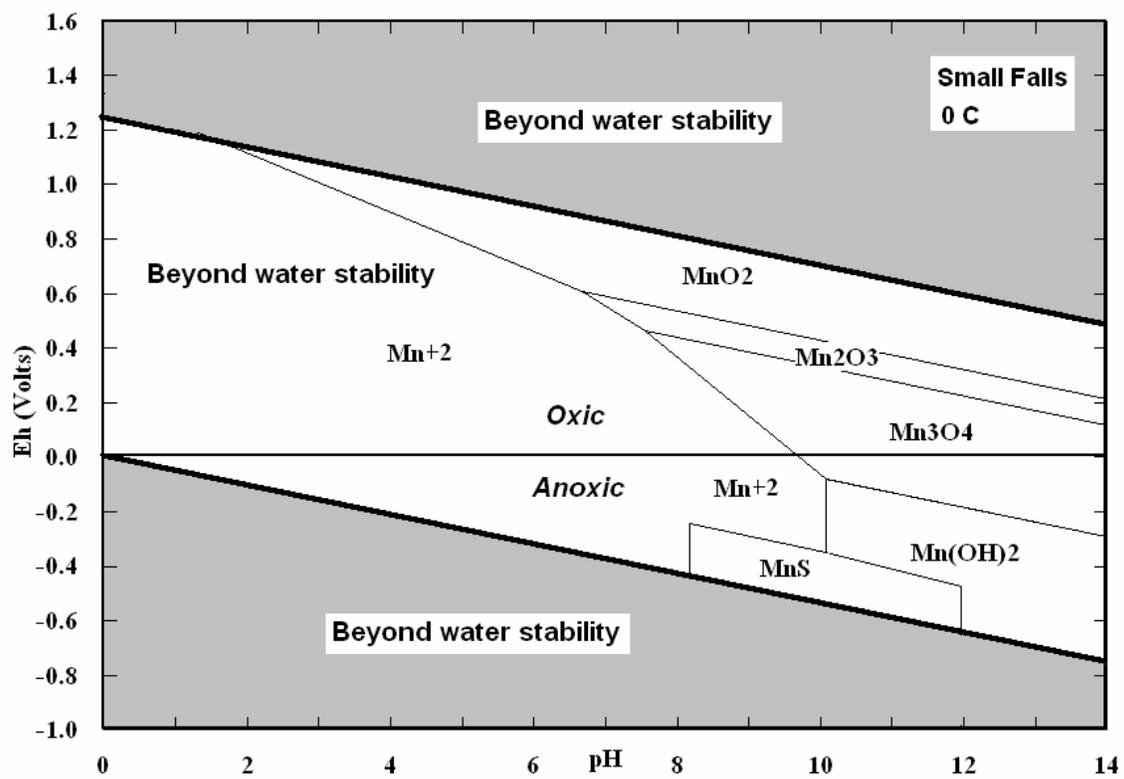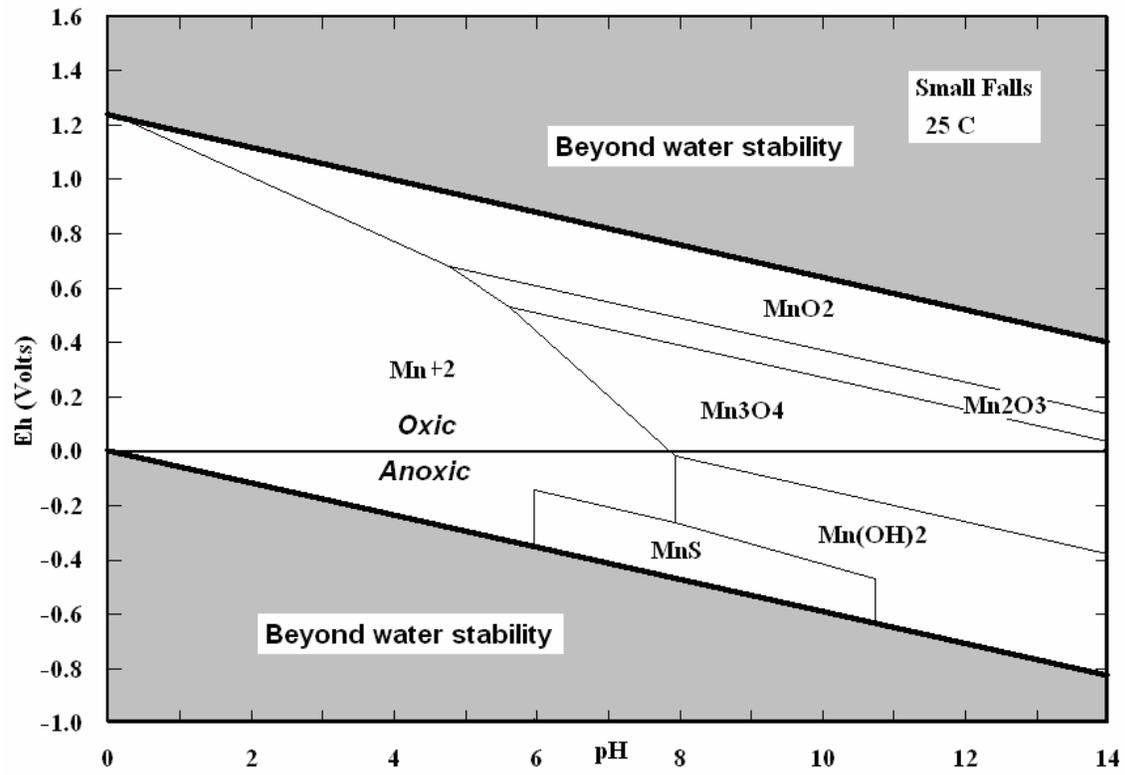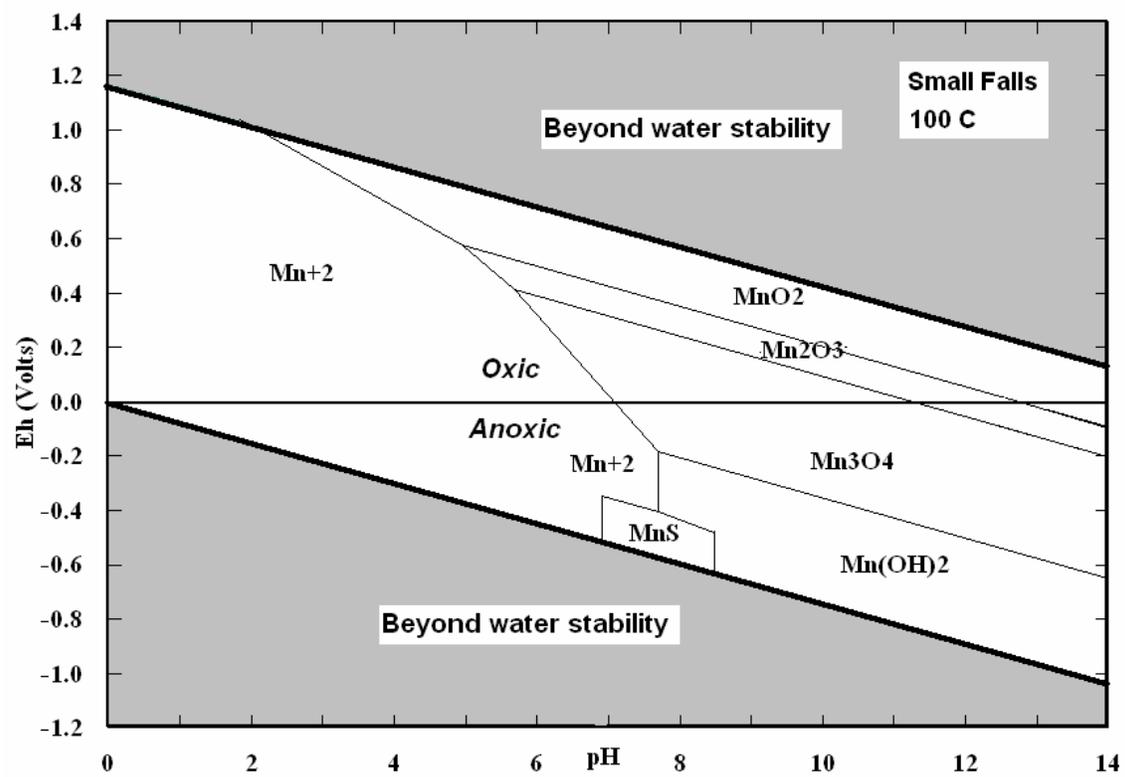
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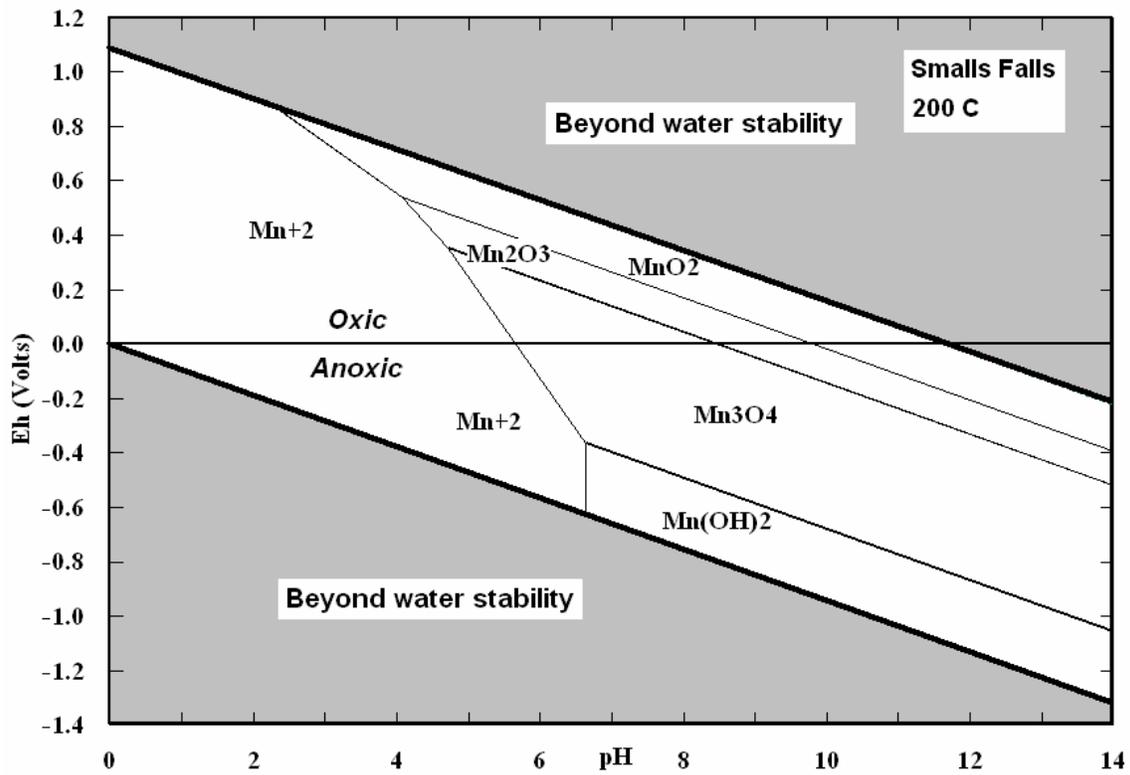
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Figure 2: Eh-pH diagrams for Small Falls concentration Mn ($8e^{-6}$ M) - Silurian sea water S ($2e^{-3}$ M). A: 0 degrees C, B: 25 degrees C, C: 100 degrees C and D: 200 degrees C.