

SHORT
COMMUNICATIONS

Possible Geochemical Conditions of Local Reducing Environments in the Earth's Crust and Upper Mantle

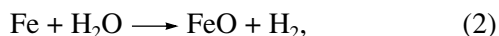
A. A. Yaroshevskii

Faculty of Geology, Moscow State University, Vorob'evy gory, Moscow, 119992 Russia

Received June 29, 2005

DOI: 10.1134/S0016702906030086

The proportion of $\text{H}_2\text{O} + \text{H}_2$ in the gas phase equilibrated with an assemblage of solid phases is buffered by the interaction with Fe, for example:



$$f_{\text{H}_2} = f_{\text{H}_2\text{O}} \cdot k_1 a_{\text{FeO}} / a_{\text{Fe}_3\text{O}_4}, \quad (3)$$

$$f_{\text{H}_2} = f_{\text{H}_2\text{O}} \cdot k_2 a_{\text{Fe}} / a_{\text{FeO}}, \quad (4)$$

and is related to the ratios of FeO (Fe) and Fe_3O_4 (FeO) activities in the solid phases at a given temperature. In a closed system, the proportion of Fe and H is set by the relative amounts of Fe, O, and H. If the amount of Fe compounds substantially exceeds the equivalent mass of hydrogen compounds, the degree of Fe oxidation, i.e., the $\text{FeO}/\text{Fe}_3\text{O}_4$ or Fe/FeO ratios, uniquely controls the ratio of H_2 and H_2O in the gas phase. This situation is characteristic of most geochemical environments of rock formation in the Earth's crust and upper mantle. When the mass of volatile hydrogen species is strongly prevalent, the $\text{H}_2\text{O}/\text{H}_2$ ratio will determine the redox potential of the system. In intermediate cases, when the equivalent masses of iron and hydrogen compounds are comparable, the mass proportions of compounds participating in reactions maybe such that the highly oxidized or, conversely, highly reduced species of Fe compounds become exhausted when equilibrium is attained. As a result, the system passes from one level of redox potential to another, which are buffered by iron compounds.

An intriguing geochemical situation can arise, if the phases selectively consuming water, e.g., a melt or serpentine, appear in the system. The dissolution of water in a silicate melt or its incorporation into the serpentine structure lead to a decrease in the H_2O activity in the gas phase and to a shift of equilibrium in reactions (1) and (2) to the left-hand side. This shift gave rise to a decrease in the amount of oxidized iron species, i.e., to the reduction of the solid phase assemblage or melt, and, in the presence of sufficient amounts of water or hydrogen, may result in the exhaustion of Fe_3O_4 in reac-

tion, (1) with the disappearance of magnetite and the appearance of metallic Fe as solid phases.

These phenomena can result in the formation of metallic iron in rocks, for example, in serpentine. Other reduced compounds of elements (carbides, metallic aluminum, and even metallic magnesium) and the accumulation of hydrogen and appearance of methane in the gas phase are also possible (see [1] for example). This shift of redox equilibria requires, first, that the total amount (mass) of hydrogen compounds involved in the interaction with a finite mass of Fe-bearing melt or rock is sufficient to bind oxygen released as a reduction product of oxidized Fe and, second, that the capacity of water consumption was high enough. These relationships may arise locally in a complex heterogeneous natural system and coexist with rocks and melts that correspond to a geochemical environment "normal" (average) in terms of redox potential. The mass proportion of water and its consumption is eventually the factor that controls the redox potential, and it is the heterogeneity of natural systems and the local fluctuations in the water-rock masses that can cause the coexistence (even within a single geological body) of mineral assemblages apparently geochemically incompatible in terms of degree of oxidation. The most spectacular example of the geochemically quite incompatible assemblages is the occurrence of metallic aluminum almost as intergrowths with olivine, a mineral whose composition includes iron oxide [2]. Such conditions cannot arise at a vast excess of water, and this is the necessary boundary condition in the open system in which the potentials of "perfectly mobile" components of the fluid phase are determined by an external infinitely large reservoir. Situations when the final result of the approach to thermodynamic equilibrium is controlled by the finite masses of components participating in the reactions can arise only in a closed system, whose size is limited by the scale of mass transfer.

It is sensible to suggest that similar environments can exist where meteoric water penetrates into the heated oceanic crust or where the mantle material experiences low-degree partial melting, when even a small amount of water contained in the mantle [3] can pro-

vide the mass proportions of the melt and gas phase required during the initial stage of melting. It is interesting that, according to the logic of the shifted phase equilibria, the development of partial melting and an increase in the melt mass should lead to the growth of the redox potential and modify the respective mineral assemblages. Therefore, there is no need to invoke, for example, the notorious flow of deep hydrogen to explain the low redox potential in equilibria of mantle mineral assemblages. Suggesting hydrogen flow is in conflict with elementary requirements of the global geochemical balance.

The shift of reaction (1) toward an increase in hydrogen fugacity should be induced by any phenomena that are accompanied by a decrease in the Fe_3O_4 activity, for example, owing to a decrease in the activity of the ferric component, due to growth in the alkalinity, in line with the principle of acidic–basic interaction [4]. Such a shift results in the disappearance of magnetite and the formation of aegirine in the mineral assemblages of apaitic rocks. Thereby, the concentration of reduced gases in the volatile phase abruptly increases [5]. Similar conditions may locally arise in the course of alkaline metasomatism, which is accompanied by the replacement of magnetite with aegirine and other minerals containing ferric ion. Again, the mass proportions of the solid and fluid phases participating in the reaction control the final result of the process. The predominant masses of iron compounds and the limited amount of hydrous fluid phase in the system is crucial for the origin of a reducing environment.

In general, the appearance of a new phase and variations in the mass proportions of coexisting phases in closed systems, in which the chemical potentials of components are determined by their variable masses in the coexisting phases, is always accompanied by a change in the thermodynamic parameters controlled by the contents of components in phases. The heterogenization (boiling) of a hydrothermal fluid might probably be of geochemical interest. The volatile components with different fugacities (solubility in the hydrous solution) will be redistributed between the newly formed

gas (vapor) phase and residual liquid, and this redistribution will be accompanied by their fractionation. In the context of redox conditions, it is interesting to consider the fractionation of $\text{H}_2\text{--H}_2\text{O}$, $\text{CH}_4\text{--CO}_2$, and $\text{H}_2\text{S--SO}_3$. A higher fugacity of hydrogen rather than water, as well as a lower solubility of methane rather than carbon dioxide in water should lead to the progressive growth of the redox potential in the gas phase, and as a consequence, in the entire system (if equilibrium is retained), in the course of the degassing of a hydrothermal solution and an increase in the gas phase/liquid solution ratio.

The local occurrence of environments controlled by geological conditions that constrain mass transfer to the fluid phase (the water/rock and liquid/gas ratios) explains the appearance of compounds stable in the Earth's crust and upper mantle at a higher hydrogen fugacity than that typical of the prevalence of water and carbon dioxide in equilibrium with "normal" mineral assemblages containing minerals with ferrous ion and magnetite.

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