

Simplified Procedures for the Estimation of the Revised-HKF Equation of State Coefficients: Concerns and Insights

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The revised-HKF equation of state describes the Gibbs free energy of aqueous electrolytes as a function of standard state Gibbs free energy, standard state entropy, temperature, pressure, and seven species-dependent coefficients (ω , a_1 , a_2 , a_3 , a_4 , c_1 , c_2). This equation is used to calculate the Gibbs free energies of aqueous electrolytes at elevated temperatures and pressures that are used to determine chemical equilibrium states for geochemical systems. The underlying theory and derivation of the HKF equation is provided in Helgeson and Kirkham (1976) and revisions to the equation are presented in Tanger and Helgeson (1988). Procedures for estimation of the equation of state coefficients are described in a series of papers [e.g. Shock and Helgeson (1988), Shock et al. (1989), Shock et al. (1997)]. These procedures are based on remarkable correlations among the equation of state coefficients. Unfortunately, many of the procedures are complex and using them efficiently requires considerable familiarity with the theoretical derivation of the revised-HKF equation of state. I will present simplified procedures for the estimation of the revised-HKF equation of state coefficients.

Before we can use empirically derived coefficients with confidence we must address the following: (1) Does the empirical generation of the equation of state coefficients surpass our ability to extrapolate meaningfully from available experimental data? (2) How sensitive is the Gibbs free energy at elevated temperatures and pressures to errors in estimated coefficients? (3) What are the cumulative effects of these errors when they are used to determine chemical equilibrium states in geochemical systems?

While these concerns must be fully addressed, it is encouraging that we can generate equation of state coefficients using simple empirical procedures. Our ability to do this may provide new insights into the fundamental thermodynamics and physical chemistry of geochemical systems. I will also present some thoughts on these insights.

Helgeson, H.C. and Kirkham, D.H (1976), *Am. J. Sci.*, **276**, 97-240.

Shock, E.L. and Helgeson, H.C. (1988), *Geochim et Cosmochim.*, **52**, 2009-2036.

Shock, E.L. et al. (1989), *Geochim et Cosmochim.*, **53**, 2157-2183.

Shock, E.L. et al. (1997), *Geochim et Cosmochim.*, **61**, 907-950.

Tanger, J.C. and Helgeson, H.C. (1988), *Am. J. Sci.*, **288**, 19-98.

Ag, Os and Ir profiles in the Massignano Eocene-Oligocene section

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Profiles of silver, osmium, iridium and some other trace elements with high stratigraphic resolution have been obtained from a short upper Eocene interval of the GSSP for the E/O boundary at Massignano, Italy (Fig.1). Five blocks, each nearly 10 cm thick from this section, and two additional samples from a core drilled in the vicinity have been analyzed. Some of these samples were split at mm scale and 12 samples were prepared. Trace elements were determined using INA technique whereas Ag, Ir and Os were determined by radiochemical analysis. The peak value of iridium is found to be 708 pg/g at 5.62 meter depth compared to about 50 pg/g far away from the peak. The peak concentration is higher than the value previously reported for this section [1]. Ir and Ag both show peak at the same horizon. The maximum concentration of Ag is 23 ng/g. The enrichment in Ir and silver at this horizon is also accompanied by simultaneous increase in Fe, Co and Cr. The Ca concentrations vary in a narrow range (29.1 to 31.8%) and cannot account for the variation in Ir concentration on a CaCO₃ free basis. Further, Ir/Fe ratio peaks at the same horizon. Four samples show Os ranging between 75 and 195 pg/g, although the errors are high (~12%). In other samples, only upper limits of Os concentration could be determined. Ir/Ag ratio at the peak is 4.5×10^{-2} which is much lower than the value of ~2.3 observed for C1 chondrites. Most of the lithophile elements (e.g. Cs, Sc, REE etc.) do not show any significant change among different samples. The chalcophile element Sb does not correlate with Ir in this section. Some of these patterns are different from those observed at K/T and P/T boundaries indicating that the sources of the anomalies in the upper Eocene are different.

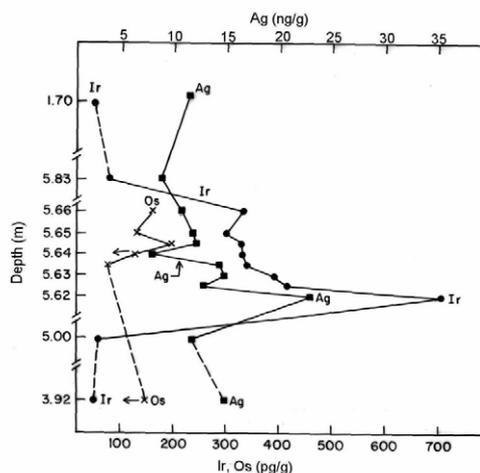


Fig. 1. High-resolution depth profile of Ir, Os and Ag in the upper Eocene at Massignano.

References: [1] Montanari A., Asaro F., Michel H. V. and Kennett J. P., (1993), *Palaio*, **8**, 420-437.