Zn-rich hercynite-magnetite assemblage in gneiss and metasedimentary rocks from Lavadores (Northern Portugal)

M.A. RIBEIRO*, H. SANT'OVAIA AND A. DÓRIA

Centro Geologia Universidade Porto, DGAOT, FCUP, R. Campo Alegre, 4169-007 Porto, Portugal
(*correspondence: maribeir@fc.up.pt)

This study describes the occurrence of hercynite in metapelitic and gneiss-migmatitic rocks outcropping in Praia de Lavadores (Northern Portugal) as metamorphic host rocks of the post-tectonic granite, 'Granito de Lavadores'. The spinel hercynite occurs mainly in pelitic and quartz-pelitic metasedimentary lithologies (micaschists and quartz-micaschists) in paragenetic association with quartz, sillimanite (fibrolite) and magnetite- ulvospinel series. In the gneiss-migmatitic rocks, the occurrence of hercynite is restricted to small restitic nodules with granoblastic texture, and is associated with magnetite-ulvospinel series, andalusite, quartz, cordierite and biotite.

The semi-quantitative mineralogical study of the hercynite has pointed out a relatively constant composition, with values of Al_2O_3, very close to 56%, FeO total between 20 and 21% and a component of ZnO between 11 and 12%. The Zn-rich hercynite-magnetite-fibrolite assemblage in the metapelitic rocks points out one of two possibilities: (i) that the biotite was consumed in a dehydration reaction, which generated hercynite, Fe-oxides Ti (magnetite-series ulvospinel) and 'melt'[1]; or (ii) that the spinel is as a result of dehydration of Zn-rich staurolite [2]. The magnetite-rich pelitic rocks, as it has already been evidenced by the high values of magnetic susceptibility and isothermal remanent magnetization curve [3], and its association with a Zn-rich spinel shows the correlation of these rocks with staurolite-rich metapelitic, occurring to the east of this coastal zone [4].The geological context, the paragenetic assemblage, either in metaspelitic or in gneiss-migmatitic rocks and the Zn-rich hercynite, indicates HT/L to MP metamorphic conditions in anomalous high thermal gradient in a late-orogenic setting. These conditions can be intensified by magmatic and/or metamorphic fluids advection over a late-orogenic period of crustal thinning, accompanied by processes of migmatization.

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A group additivity approach to describe the complexation of radionuclides by fulvic acids in geochemical modeling studies

LAURENT RICHARD[1], CAROLINA SABATER[1], AMBROSE KIPROP[2,3], EMILIE POURTIER[3] AND CHINH NGUYEN-TRUNG[3]

[1]Amphos21, Pg. García i Fària 49-51, 08019 Barcelona, Spain, laurent.richard@amphos21.com
[2]Moi University, Department of Chemical and Process Engineering, P.O. box 3900, 30100 Eldoret, Kenya
[3]Nancy-Université, G2R, 54506 Vandoeuvre-lès-Nancy cedex, France

Clay formations which are considered by a number of countries as potential sites for high-level nuclear waste storage often contain a significant amount of organic carbon mostly present under the form of kerogen. A possible scenario considered in feasibility studies for nuclear waste storage is water seepage through the concrete walls of a storage site. It has been shown that complex mixtures of soluble (including fulvic acid-like) organic compounds are generated from kerogens under conditions of alkaline perturbation [1]. These organic compounds are potentially able to complex and transport radionuclides around nuclear waste disposal sites. Knowledge of the equilibrium constants of complexation reactions of radionuclides by fulvate anions is therefore of primordial interest for performance assessment exercises.

New developments in analytical chemistry have resulted in improved knowledge of the molecular structure of fulvic acids [2]. Structural models of individual fulvic acids have been proposed [3], for which thermodynamic properties can be estimated using group additivity techniques (e.g. see [4]). Equilibrium constants at infinite dilution published in the literature for complexes of radionuclides with low-molecular-weight organic compounds can be used to develop group additivity algorithms for calculating the standard molal Gibbs energies of formation of radionuclide-fulvate complexes. The latter properties can help in the interpretation of laboratory experiments on the complexation of radionuclides by natural organic matter. They can also be incorporated in geochemical models of nuclear waste repositories.

[1] Claret *et al.* (2003) *Sci. Total Environ.* **317**, 189-200. [2] Sutton and Sposito (2005) *Environ. Sci. Technol.* **39**, 9009-9015. [3] Stenton *et al.* (2003) *Anal. Chem.* **75**, 1275-1284. [4] Amend and Helgeson (1997) *Geochim. Cosmochim. Acta* **61**, 11-46.