

Many-body effects in XPS and chemical bonding

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A major goal with x-ray photoelectron spectroscopy (XPS) is to derive both the character of chemical bonding and valence states from the spectra. Ionic compounds, especially oxides, often have complex and intense satellite features that arise from a combination of inter-atomic and intra-atomic many-body effects that can reflect both bonding and oxidation state. [1] While multiplet splittings arise dominantly from the open-shell structure within the ionized atom, [2] inter-atomic many-body effects may also make important contributions to the satellite structure. [1] Although these inter-atomic effects have been studied extensively, a quantitative and definitive connection between the relative energies and intensities of the satellites on the one hand and both the extent of covalent bonding and oxidation state on the other, has not been established. In the present work, we consider two oxides, UO_3 and CeO_2 , where the metal cations are closed shell, which increases the importance of inter-atomic relative to intra-atomic many body effects. The CeO_2 satellites are intense while the UO_3 satellites are weak. We have established relations between the satellite energies and intensities with the extent of the covalent bonding. This theoretical information has been obtained using relativistic many-body molecular orbital wavefunctions. With these wavefunctions, the covalent character of the orbitals arises naturally. This work is an important step toward inferring material properties of interest to both geochemistry and more generally chemistry from the XPS satellite structure. This research was supported, in part, by the Geosciences Research Program, Office of Basic Energy Sciences, U. S. Department of Energy (DOE) and Geosciences Research Program, Office and, in part, by the German Science Foundation (DFG).

[1] Bagus *et al.* (2010) *Chem. Phys. Lett.* **487**, 237-240. [2] Bagus & Ilton, (2006) *Phys. Rev. B* **73**, 155110.

Whole rock and mineral composition constraints on the genesis of the giant Hongge Fe-Ti-V oxide deposit in the ELIP, SW China

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The Hongge giant Fe-Ti-V oxide ore deposit, related to a plume activity (~260 Ma), is hosted in a layered intrusion located in the central part of the Emeishan Large Igneous Province (ELIP), SW China. Most of the economic Fe-Ti-V oxide ore layers occur within the middle clinopyroxenite zone of the intrusion. Opinions on the origin of the oxides vary from oxide-silicate liquid immiscibility to accumulation of titanomagnetite crystallizing from a basaltic magma.

Our new results favor the crystallization model. The occurrence of multiple Fe-Ti oxide layers within a single cyclic unit and the repetitive appearance of sulfide, olivine and Cr-rich magnetite in the base of each cyclic unit suggest that multiple pulses of magma was involved in the formation of the Hongge Fe-Ti-V oxide deposit. Magnetite and coexisting olivine in the Hongge deposit have much higher MgO contents than those in other oxide deposits associated with large layered intrusions in the world, underscoring the importance of relatively primitive parental magma and relatively early saturation of titanomagnetite in the magma in the formation of the giant Fe-Ti-V oxide deposits in the ELIP.

Phase equilibrium constraints suggest that the Hongge parental magma is similar to that of some most primitive Emeishan high-Ti basalts. Depletion of incompatible trace elements in the oxide ores and associated rocks in the intrusion as compared to the coeval high-Ti basalts suggest that not all the magma involved in development of the Hongge intrusion has been retained. We propose that this intrusion was a magma conduit and that some of the liquid was lost to the peripheral sills, shallower intrusions or lavas.