

Thermodynamic properties of hydration layers on surfaces of metal oxide nanoparticles

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Water is ubiquitous on the surface of oxide nanoparticles and can exert a profound influence on the thermodynamic properties of the oxide [1]. We have measured inelastic neutron scattering (INS) spectra for several hydrated metal oxide nanoparticles systems, including 6nm SnO₂, 7nm rutile-TiO₂, 16nm Co₃O₄, and 10nm CoO, and determined the isochoric heat capacity and vibrational entropy of the water confined to their surfaces [2-4]. The results from these studies have been combined with complementary calorimetric data and show that the surface energy of the underlying metal oxide particles exerts a strong influence on the heat capacity of the hydration layers. The surface water adsorbed on metal oxide nanoparticles with higher surface energies have lower heat capacities and vibrational entropies. For example, isostructural SnO₂ and rutile-TiO₂ have surface energies of 1.72±0.01 and 2.22±0.07 Jm⁻², respectively, with S₂₉₈ values of their hydration layers equal to 37.17 and 32.34 JK⁻¹mol⁻¹, respectively [3, 5]. In addition, Co₃O₄ spinel and CoO rocksalt nanoparticles, although chemically similar, have surface energies of 1.96±0.05 and 3.57±0.20 Jm⁻², respectively, with S₂₉₈ values of their hydration layers equal to 38.13 and 37.03 JK⁻¹mol⁻¹, respectively [4, 5].

[1] Boerio-Goates *et al.* (2006) *Nano Lett.* **6**, 750.

[2] E.C. Spencer *et al.* (2009) *J. Phys. Chem. A*, **113**, 2796.

[3] E.C. Spencer *et al.* (2011) *J. Phys. Chem. A*, submitted.

[4] E.C. Spencer *et al.* (2011) *J. Phys. Condens. Matt*, in press.

[5] A. Navrotsky *et al.* (2010) *Science* **330**, 199.

The Late Jurassic Andean back-arc volcanism, Northern Chile (26-31°S)

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The configuration of the Andes in southwestern Gondwana during the Jurassic and Early Cretaceous was characterized by abundant primitive arc magmatism, and marine to continental extensional back-arc basins controlled by hemigraben fault systems. Occasional effusion of volcanic material occurred along the eastern flanks of these basins. Between 26° and 31°, two parallel belts of volcanic rocks crop out to the east of the contemporary Upper Jurassic arc. The volcanic rocks located closer to the arc (G1), have a maximum age of 163.2 Ma, range from basaltic-andesite to andesite, with minor rhyolites, and have calc-alkaline affinities but with higher alkali content than the arc rocks. The more distant volcanics (G2) have a maximum age of ca. 153 Ma and are mostly alkaline basalts.

Spider diagrams show enrichment in LILE, usually not higher than 100, relative to the primordial mantle, and concentrations of HREE below 10. The rocks of G1 are characterized by Nb-Ta troughs and La_n/Nb_n ratios between 2.2 and 8.1, while G2 trace elements patterns have a concave-down shape, similar to that of the OIB, and La_n/Nb_n ratios between 1.8 and 2.5 or Nb-Ta anomalies commonly absent. Rocks from both groups have flat REE patterns, with minor negative Eu anomalies for G1, and positive Eu anomalies for some G2 lavas. The Ni concentrations (44-223 vs 20-130 ppm), Dy/Yb (1.8-2.8 vs 1.9-2.1) and La/Yb (7-23 vs 8-17) are higher for the G2 lavas, which is consistent with the greatest distance of this group from the trench, and lower degrees of partial melting of their mantle source. The lower Nb/Yb for the G1 lavas (2-37 vs 3-8) suggests a more depleted source than that of the G2 lavas, but more enriched relative to the source of the arc rocks (0.1-3). Isotopic ratios (⁸⁷Sr/⁸⁶Sr=0.7035-0.70501, ¹⁴³Nd/¹⁴⁴Nd=0.512455-0.512742, ²⁰⁶Pb/²⁰⁴Pb=18.4-19.34, ²⁰⁷Pb/²⁰⁴Pb=15.6-15.67, ²⁰⁸Pb/²⁰⁴Pb=38.43-39.0) are indicative of an enrichment in the magma source from the arc eastwards; the spatial and temporal geochemical variations suggest progressive increase of lithospheric contributions to the back-arc magmatism.