Calcium-(bi)carbonate equilibria in aqueous solutions: a high-accuracy titration-based study

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A thorough understanding of calcium-(bi)carbonate equilibria in aqueous solutions is key for making accurate predictions of aqueous speciation in Ca-HCO_3-CO_3-H_2O-CO_2 systems and assessing the extent of precipitation (or dissolution) of $CaCO_{3(s)}$ polymorphs in environmental, biological, and industrial systems. Despite earlier determinations of the formation constants of calcium-(bi)carbonate ion pairs in aqueous and seawater-like solutions, recent studies postulating the formation of metastable [1,2] or stable prenucleation $CaCO_3$ nanoclusters [3,4] have triggered new interest on calcium-(bi)carbonate interactions, particularly at near-calcite saturation conditions. Moreover, anomalous pH values and calcium concentrations consistently observed during acidimetric titrations of aqueous calcite suspensions suggest that the chemical equilibria governing the $CaCO_3$-HCO_3-CO_3-H_2O-CO_2 system may not be fully understood [5].

In this study we perform a critical review of the available thermodynamic constants describing the formation of calcium-(bi)carbonate ion pairs and compare these values with constants extracted from new experimental data acquired over fairly broad compositional ranges. Our experimental approach consists of performing high-accuracy titrations of (bi)carbonate solutions in contact with a gas phase but completely isolated from the atmosphere. For the first time in this type of determinations, $CO_{2(g)}$ exchange across the gas-water interface is quantitatively monitored and the chemistry of the solution is fully characterized (analytically overdetermined) through a combination of pH, alkalinity, pCO_2, ΣCO_2 pCa, and ΣCa measurements at each titration point. Data fitting and parameter extraction is made stochastically following a genetic algorithm approach described earlier [6].

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Leachate analyses of volcanic ashes from Sakurajima volcano, Japan: insights into the magmatic degassing processes

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Ash erupted from active vents acts, by adsorption onto its surface in volcanic plumes, as an efficient scavenger of volatile elements such as sulphur (as sulphate, SO_4^{2-}), halogens, and other species present as soluble salts adhering to the particle surface. Analysis of water-soluble ash leachates is a suitable supplement for remote monitoring of volcanic gases at inaccessible volcanoes. The chemical composition of ash leachates is considered as a proxy for volcanic plume chemistry (volatile ratios), and its temporal variations reflect changes in the magmatic conditions, eruptive activity, along with local conduit- and plume-related processes. The importance of ash-leachate analysis also lies in the fact that up to 30-40% of the volatile budget emitted by subduction-related volcanoes are scavenged by such adsorption processes on volcanic ash. This adsorbed component has been generally neglected, resulting in excess degassing underestimated by 30-40%.

In this study, we investigate the temporal variations of the chemical composition of water-soluble leachates from volcanic ashes emitted from Sakurajima volcano, Southern Kyushu, Japan, during the period 1981-2011 (with emphasis on 2010-2011). Pristine ash was collected on-site, ca. 3 km away from the vent, directly after an explosion occurred.

We observe a strong positive correlation between SO_4, F and Cl/SO_4 against Cl, especially in ash leachates from 2008 to 2011, corresponding to the reactivation of Showa vent. Our results also show significant long-term and short-term temporal variations in ash leachate compositions (SO_4, F, Cl, Cl/SO_4, S/F, Mg/Na), reflecting changes in the eruption rate and style. Since ash-gas interactions started at the fragmentation level within the vent, these temporal variations may also reflect changes in the fragmentation mode or the volatile accumulation (adsorption) process onto the ash within the vent. In turn, this is linked to the mean residence time of magma in the upper conduit (including the vent), as a response to magma renewal and/or convection in this part of the volcano system.

In addition to chemistry we also investigate the influence of grain size distribution and texture on ash-leachate analyses over time. This is at present time very preliminary, but if correlations are found in particular between volatile ratios in ash leachates and the grain size and/or texture, it will provide new and valuable semi-quantitative information on the degassing processes in the shallow volcanic conduit.