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Vanadium in Al-ore (bauxite) from mines of central Greece

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Vanadium, either as critical metal extracted as by-product of other metal ores (e.g., [1]) or as potential hazardous element due to its involvement in red mud (RM) accident in Hungary (e.g., [2]), is an element of increased importance in aluminum mining and metallurgical industry. Recently, seawater-leaching experiments indicated significant V release from Greek RM and negligible for its parent Al-ore (bauxite) [3]. Acetic acid-leaching tests with the RM also indicated V release, as in the case of seawater [3]. While there is much debate on V in Hungarian, Greek and Australian RM [2-4], there are no advances concering its partitioning and speciation in the mineral phases of bauxite. Commercial bauxite samples from mines of central Greece have been investigated -in bulk- by PXRD (incl. the clay fraction of 2-0.2µm) and ICP-MS, as well as, at the micro-/nano-scale using electron microscopy (SEM-WDS and TEM/HRTEM, after FIB-SEM -in selected areas previously checked by WDS- and Ar ion milling for microstructure observation) along with Synchrotron radiation (SR $\mu\text{-}XRF$ and $\mu\text{-}XAFS).$

The measurements showed that V is mainly intercorrelated to Si, Ca and Mg (not to Al, Ti, Fe) in microareas between pisoliths, following the Si/Al ratio. The hosting phase is most likely a kaolinite-type clay (V up to 1400 ppm), and less probably boehmite. It predominantly occurs as V⁵⁺ (although minor contribution of V⁴⁺ cannot be excluded), indicating the existence of adsorbed V-anions, belonging to the series of metavanadate (VO₃⁻) to decavanadate (V₁₀O₂₈⁶⁻), rather than V-cations of lower oxidation state (V⁴⁺/vanadyl/oxovanadium or even V³⁺) substituting Al³⁺ into the octahedral sheet of kaolinite-type structure [5,6]. It is therefore demonstrated that V is not related to Fe- and Fe-Ti-oxide minerals, despite their abundance in Al-ores, in contrast to its behaviour in other common basic metal ores [6].

Mudd *et al.*, (2016 – in press) Ore Geol. Rev.; [2]
Burke *et al.*, (2013) Environ. Sci. Technol., **47**, 6527; [3]
Gamaletsos *et al.*, (2016) Sci. Rep., **6** (21737), 1; [4] Gräfe *et al.*, (2011) J. Environ. Quality, **40**, 767; [5] Gehring *et al.*, (1993) Clays Clay Mineral., **41**(6), 662; [6] Huang *et al.*, (2015) Chem. Geol., **417**, 68.