

Elemental composition of jarosite from gossan and acid rock drainage in the Río Tinto mining basin, Spain

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Jarosite is an Fe hydroxysulfate mineral that is commonly formed in acidic environments, often following pyrite weathering. Jarosite minerals have the formula $AB_3(TO_4)_2(OH)_6$ where A is most often occupied by K^+ , Na^+ or H_3O^+ , B is mostly occupied by Fe(III) and T is mostly occupied by S(VI), although many other element substitutions are possible. In the Río Tinto mining basin, jarosite is found within weathered gossan, on freshly exposed pyrite-bearing rock faces and in waterways that drain from the mining areas. In these environments, the role of jarosite as a sink for trace and major elements can be difficult to directly determine by elemental analysis of dissolved solids, due to contamination by co-occurring mineral phases. Microanalytical techniques such as energy-dispersive X-ray spectroscopy (EDX) can identify elements associated with jarosite but cannot provide conclusive evidence of isomorphic substitution. Some previous investigations of natural jarosite from the Río Tinto area have used X-ray diffraction (XRD) analysis of the unit cell size to identify the major elements that occupy the A, B and T sites [1,2]. However, the determination of elemental substitution based on the unit cell parameters alone is an underdetermined problem, because the unit cell of jarosite can only be fitted in two dimensions (the angles α, β and γ are fixed and the dimensions have the relationship $a=b \neq c$) and a larger number of element substitutions may affect the unit cell. By supplementing measurements of the unit cell with spectroscopic analysis of structure, e.g. by Raman Spectroscopy, and cross correlating the signatures of element substitution, it is possible to see that trace elements such as Pb also affect the mineral structure of natural jarosite, including in jarosite formed in rivers where only K-, Na- and H_3O -jarosite have been previously identified. The results highlight the importance of jarosite for trace metal mobility in the Río Tinto mining basin and demonstrate how the elemental composition of jarosite in various natural environments can be determined by combining analysis methods of mineral structure.

[1] Basciano & Peterson (2007) *Am. Mineral.* 92(8-9), 1464-1473.

[2] Fernández-Remolar, Morris, Gruener, Amils & Knoll (2005) *Earth Planet. Sci. Lett.* 240(1), 149-167.