The largest mercury anomaly on Earth (Almadén, Spain): a mantle-derived feature?

La mayor anomalía de mercurio en la Tierra (Almadén. España): ¿un proceso de origen mantélico?

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Abstract

The Almadén Hg deposits are associated with deeply altered magmatic rocks, which main features are briefly described here. Geochemical, including isotopic, data on these rocks suggest that they are derived from deep mantelic sources. The volcanic units underwent low-pressure alteration processes, probably related to the geothermal evolution of the district along with the magmatic activity (Silurian-Devonian). As a conclusion, this magmatism could have been the responsible for the mobilisation of mercury concentrated in the district deposits.

Resumen

Se describen en el presente trabajo las características de las rocas magmáticas con las que aparecen relacionadas las mineralizaciones de mercurio del distrito de Almadén, y los procesos de alteración que las afectan. Los datos geoquímicos e isotópicos referidos a estas rocas indican que proceden de fuentes mantélicas profundas. Las unidades volcánicas sufrieron procesos de alteración a baja presión, probablemente relacionados con la evolución geotérmica del distrito durante el propio periodo de actividad del magmatismo (Silúrico-Devónico). Se concluye que este magmatismo puede haber sido el responsable de la movilización del mercurio que constituye los yacimientos del distrito.

Key Words: *magmatism. alterations. Hg deposits. Hercynian. Almadén. Spain.*

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Introduction and geological setting

Almadén (central Spain) (Fig. 1) is the most remarkable mercury mining district in the world, having produced one third of the total world production of this element, and can be regarded as the largest mercury anomaly on earth. The volcanic-related mercury ore bodies are hosted by a lower Paleozoic sequence comprising sedimentary and volcanic rocks, which unconformably overlies the pre-Ordovician basement of the Central Iberian Zone of the Iberian Variscan Chain. What makes Almadén a truly remarkable case is the long-lasting (Ordovician to Devonian), intraplate, mantle-derived persistent alkaline to tholeiitic magmatism (Higueras, 1995) (Fig. 2), which concentrated nevertheless in a extremely small area, i.e., the so-called Almadén Syncline (~60 x 20 km).

The magmatism

The stratigraphic record of the area comprises several packages of black shale and sandstone/quartzite units, including frequent intercalations of submarine mafic alkaline volcanic rocks with ultramafic xenoliths, diatreme-type intrusive breccias observed throughout the stratigraphic column, and intrusive dolerites of tholeiitic affinities. An interesting feature of the Almadén magmatism is its high CO_2 content. Most of the basic volcanic rocks in the district display CO_2 values from 8 to 15%, reaching values as high as 20% and 30% (basalts and ultramafic xenoliths, respectively) (Higueras, 1995). Although these values could be of secondary origin, the fact of the high explosivity of the volcanism (recorded all along the stratigraphic record; diatreme intrusive breccias), together with the isotopic composition of these carbonates ($\delta^{13}C_{range}$ = -3 to -9; dolerites, basalts, diatremes, Hg veins) (Eichmann *et al.*, 1977; Rytuba et al., 1988), indicate a primary and possibly mantellic origin for this component.

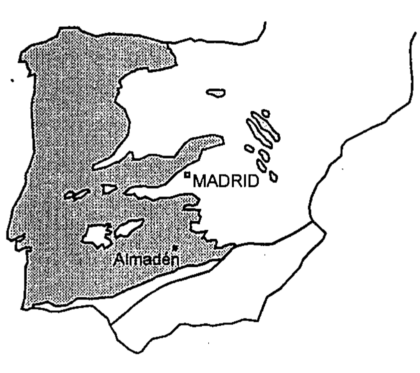

Figure 1.- Location of Almadén in a geological sketch map of Iberia. Shadowed: Iberian Variscan chain.

Figura 1.- Situación de Almadén en un esquema geológico del Macizo Ibérico. Sombreado: cadena hercínica Ibérica.

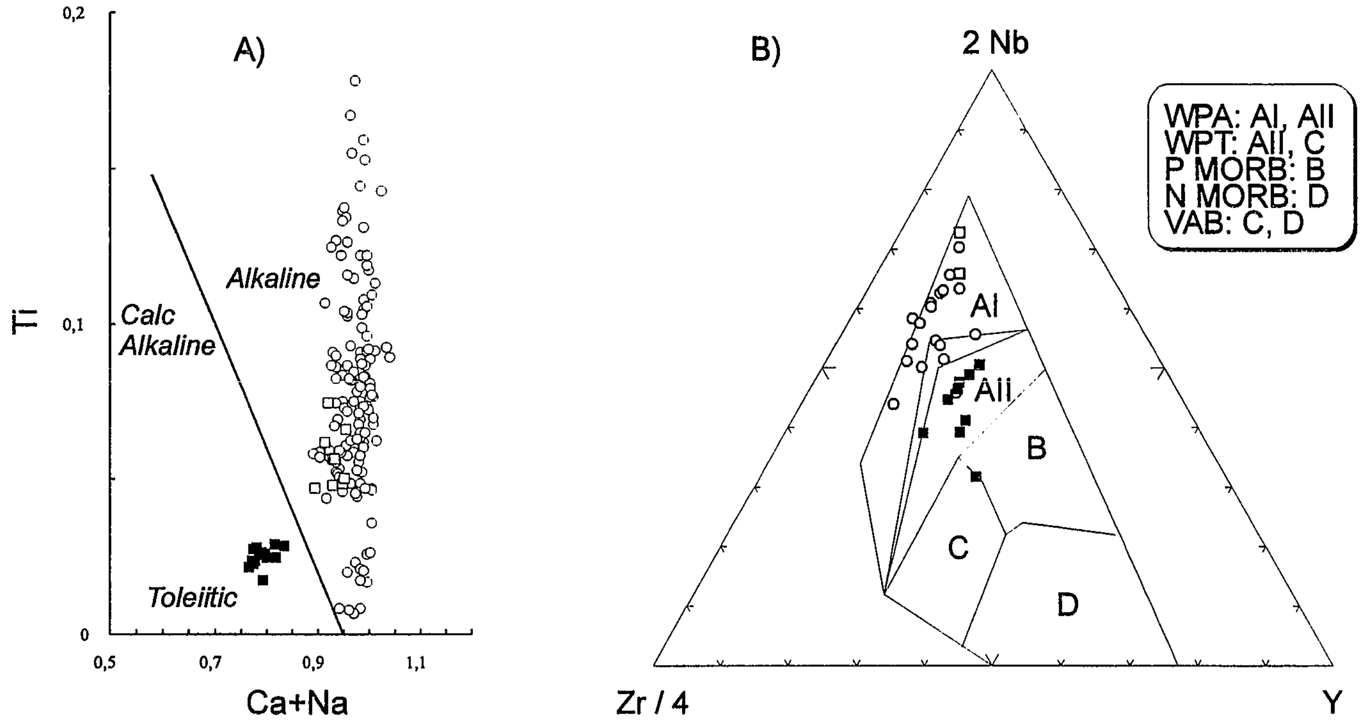

Figure 2.- A) Ca+Na *vs* Ti diagram (Leterrier *et al.*, 1982) for pyroxenes from basic magmatic rocks in the Almaden district. Open circles: Basalts; black squares: dolerites; field A: pyroxenes from alkaline rocks; field CA: pyroxenes from calc-alkaline rocks; field T: pyroxenes from tholeiitic rocks. B) 2Nb:Zr/4:Y Diagram (Meschede, 1986) for the whole rock composition of basic magmatic rocks of the Almadén district. WPA: Within-plate alkaline basalts; WPT: Within-plate tholeiites; P MORB, N MORB: Mid-ocean ridge basalts; VAB: Volcanic arc basalts. Symbols, as in figure 2A.

Figura 2.- A) Diagrama Ca+Na vs Ti (Letterier et al., 1982) para los piroxenos de las rocas magmáticas del distrito de Almadén. Círculos blancos: basaltos; cuadrados negros: diabasas; campo A: piroxenos de rocas alcalinas; campo CA: piroxenos de rocas calcoalcalinas; campo T: piroxenos de rocas toleíticas. B) Diagrama 2Nb:Zr/4:Y (Meschede, 1986) para la composición geoquímica de las rocas magmáticas básicas del distrito de Almadén. WPA: basaltos de intraplaca; WPT: Toleitas de intraplaca; P MORB, N MORB: basaltos de dorsales oceánicas; VAB: basaltos de arcos volcánicos. Símbolos, como en 2A.

Geophysical data and surface mapping show that the mafic volcanism within the Almadén syncline was by far more important than elsewhere in the Iberian plate. The magmatic record is almost continuous and evolved from earlier widespread basanitic-nephelinitic and alkali-olivine basaltic extrusions, mostly into the Silurian-Devonian part of the section, to late transitional/tholeiitic intrusive dolerites, which are scattered throughout the whole sequence. The petrological study (Higueras, 1995) indicates an evolving environment for the magmas formed in the Almadén syncline. The source may have been an enriched asthenospheric mantle, getting progressively depleted in the least incompatible elements. The Silurian basic rocks represent liquids formed by the lowest partial melting rates (1.6-6%), which increased in the Devonian basic rocks (4-9%), and reached its higher values in the late subvolcanic tholeiites (10-17.5%) (Higueras and Munhá, 1993; Higueras, 1995).

Long-lasting submarine hydrothermal alterations

Basalts and dolerites underwent regional hydrothermal alteration, contemporaneous with water-cooling on the seafloor, being pervasively transformed to spilite-type albite-chlorite-carbonate rich basalts. These alteration facies developed within a geologic environment undergoing geothermal-type alteration processes, under submarine conditions. High-geothermal gradients were provided by coeval magmatic activity, the whole process probably lasting from the early Silurian to late Devonian, where most of the effects of low-grade regional alteration and magmatic activity concentrate (Hall *et al.*, 1997; Higueras *et al.*, 1998). P-T conditions for this hydrothermal system are constrained by the geological environment in which developed. Thus by late Devonian, when magmatism and marine conditions were vanishing, we can assume hydrostatic (top of the system) to suprahydrostatic conditions (bottom) with a maximum pressure of ~ 40 MPa (400 bar) (Sibson, 1990). This is to be regarded as a maximum estimate, when the volcanic-sedimentary pile reached its maximum thickness (~ 3 km., García Sansegundo *et al.*, 1987). A comparison of the Almadén alteration facies to those of modern geothermal analogous (e.g., Iceland geothermal fields, Liou *et al.*, 1987; Yardley, 1989) suggest steep geothermal gradients and mineral formation within the range ~ 200°-300°C.

Origin of the mercury

Derivation of the Almadén Hg from sediments (Ordovician black shales) has been advocated by Saupé (1990), who also refuted a mantle origin. However, recent work indicates a close relationship between the mercury deposits and the lower Paleozoic alkali basaltic volcanism in the Almadén basin (Higueras, 1995). Clearly, the huge, unique, Almadén Hg deposits should have required exceptional conditions to their genesis. We suggest that such a world-class geochemical anomaly may ultimately reflect the characteristics of the mantle source for the alkali basaltic magmas. Indeed, mantle metasomatic activity and the low degrees of partial melting inherent to the genesis of the Almadén mafic magmas could have converged to provide an efficient mechanism for Hg pre-enrichment in the basaltic rocks (e.g., Dromgoole and Pasteris, 1987).

Conclusion

The geologic, mineralogic and isotope data (Higueras, 1995; Higueras and Munhá, 1993; Higueras *et al.*, 1998; Hall *et al.*, 1997) suggest that long-lasting submarine magmatic activity in the Almadén basin may have triggered persistent submarine hydrothermal activity along most of the Silurian and Devonian, i.e., a timespan of about 70 Ma, and suggest a magmatic origin for mercury. Submarine geothermal activity would then have established the necessary links between early and late sulfide deposition, isotopic multiple source signatures, and the original mantle source of Hg in the Almadén deposits.

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