A radium and radon investigation of the submarine estuary under Venice

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Submarine groundwater discharge (SGD) is now recognised as a major pathway for nutrients and contaminants. Mass balance models based on excesses of natural radioactive isotopes in coastal environments (estuary, lagoon) can provide integrated estimates of SGD. In this work, we measured ²²⁶Ra and ²²²Rn activities in the southern part of the Venice lagoon, a most emblematic case of highly vulnerable coastal flatland heavily impacted by anthropogenic activities.

²²⁶Ra activities measurements were performed by isotope dilution and thermal ionization mass spectrometry on small samples (0.5L). Very small variations in ²²⁶Ra can be resolved by this technique, thanks to the high precision that is attainable (1 to 5% on 20 to 200 fg samples). ²²²Rn activities were measured by in-situ continuous-monitoring α-counting technique with a precision of 10%.

 ^{226}Ra and ^{222}Rn activities are significantly higher in the lagoon samples (2.3-5.3 and 26-82 Bq/m³ respectively) than in the open Adriatic Sea (2.2 and 10 Bq/m³ respectively). Mass balance models taking into account riverine inputs, diffusion from sediments, loss, production and decay of the isotopes, do not explain the lagoon excesses and suggest the existence of another source of ^{226}Ra and ^{222}Rn in the lagoon.

Groundwater from the semi-confined aquifer (0-30 m) connected with lagoon waters presents significant enrichment in 226 Ra and 222 Rn (c.a. 35 Bq/m³ and 1300 Bq/m³), and may be considered as an additional source to generate the required excess. Using these activities, the input of groundwater necessary to explain the observed excess in the lagoon is 5.2×10^5 and 5.5×10^5 m³.d⁻¹, based on 226 Ra and 222 Rn mass balance respectively. Furthermore, Rn monitoring during tidal cycles shows that the excess activity is produced during the falling tide, when aquifers significant discharge interstitial waters through the sediments.

References

Moore W. (1996) *Nature* **380** 612-614. Burnett W.C. *et al.* (2006), *Sci Total Environ.* **367** 498-543.

Cryptic zoning in garnets from the Nufenen Pass area

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Garnets from graphite rich black shales of the Mesozoic cover of the Gotthard Massif in the Swiss Alps display textural sector zoning with birefringent lamellae emanating from sector boundaries. Central sections of garnets cut along [110] display 6 sectors, which are in places crowned by a graphite rich cap. The birefringent lamellae are oriented normal to the sector end face. Individual lamellae have a length of up to 300 microns and a thickness of typically 10 microns. The lamellae have an elliptical cross section of a few tens of microns for their long axis on sections parallel to the sector end face. A cross hatched pattern is created with lamellae orientations parrallel to the edges of the sector walls. Lamellae are absent in the graphite inclusion rich rim. EPMA analysis of the birefringent lamellae show that they are Ca richer than the adjacent isotropic lamellae which are Fe richer. The composition difference in calcium and iron between the two type of lamellae can be up to 0.2 cation per formulla unit. The lamellae are zoned along their length, following the overall garnet zoning pattern. Composition ranges for the two lamellae overlap for a single garnet.

The coexistance of two garnet composition and structure could be explained by a miscibility gap in the solid solution or by crystallisation of one or two metastable precursors. The composition difference between the two type of lamellae is too small to reflect a miscibility gap and lamellae composition overlap. Hence they are not exsolutions. Other type of zoning have been explained by the replacement of heterogeneities in the matrix or concentric zoning due to rythmically changing conditions (Yardley *et al.*, 1996). The crystallographic orientation of the lamellae indicates that they do not represent replacement of matrix heterogeneities. The orientation of the lamellae indicates that types of lamellae were crystallizing.

We propose an alternate mechanism for this case. Two garnets with a slightly different composition and structure nucleate topotactically on the surface of a growing garnet with a similar probability. It is enough that continued nucleation of a new garnet layer slightly prefers the same structure to assure a fiber-like growth of both compositions side by side.

Reference

Yardley B.W., Condliffe E., Lloyd G.E., Harris D.H.M. (1996). Eur. J. Mineral. 8, 383-392.