Pd diffusion into pentlandite evidence from laser ablation

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Many magmatic ore deposits are zoned with an Fe-rich portion and a Cu-rich portion. Nickel is generally evenly distributed. This distribution is attributed to fractional crystallization of a sulfide liquid, with Fe-rich monosulfide solid solution (Fe-mss) crystallizing first and forming an Fe-rich cumulate. The fractionated liquid eventually crystallizes as Ni-rich mss (Ni-mss) and a Cu-rich intermediate solid solution (iss). Rhenium, Os, Ir, Ru and Rh concentrate in the Fe-rich rocks. Platinum, Pd and most other chalcophile elements concentrate in the Cu-rich rocks. From 600 °C pyrrhotite (Po) and pentlandite (Pn) exsolve from mss and chalcopyrite (Ccp) exsolves from iss. Much of the Pd is hosted in Pn. This is conterintuitive because Pd is incompatible with mss ($D^{Mss/Liq} = 0.2$). Thus one would expect the Pd to concentrate in the Cu-rich liquid and partition either into the iss or, if it is incompatible with iss, then it should crystallize as a Pd mineral. In order to explain this conundrum we have previously proposed that Pd diffuses into the Pn during the exsolution process.

To investigate the affects of diffusion we have determined the Pd content of Pn both from Fe-rich and Cu-rich ore, looked at the variation of Pd content in Pn with texture and at the zonation of Pd within Pn. During cooling and exsolution the texture of Pn changes. The Pn formed at high temperature is coarse grained and granular, the Pn formed at lower temperature forms narrow chains around the Po and the Pn formed at the lowest temperatures occurs as small flames within Po. The granular Pn is richest in Pd, the flames poorest in Pd. Furthermore the granular Pn is zoned, with highest concentrations in the center. We interpret these observations to suggest that the Pn that formed at high temperature (the center of the granular Pn) absorbed most of the Pd in its viscinity leaving a depleted halo around it. Thus the next layer of the granular Pn that formed was depleted in Pd. The chain Pn and flame Pn that form at lower temperatures contains less Pd for three reasons: the granular Pn had depleted the sulfides in Pd; the temperature was lower and hence diffusion is slower; there was less time for diffusion to occur before diffusion ceases altogether.

The Ca-carbonate bio crystal status in mollusk seashells revisited

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A better understanding of the bio-controlled mineralization process requires first a careful characterisation of bio crystalline matter at all scales. Thus we report on TEM and AFM imaging of various fresh bivalve and gastropod shells, while avoiding at our best misleading artefacts due to sample preparation and observation.

Results and discussion

Supramicronic shell microstructures like fibers, tablets and prisms [1] are all granular, as made by bridged monocrystalline rounded granules $\approx$ 150-500 nm in size, encapsulated in an organic membrane (Fig. 1). They form 1D, 2D and 3D interconnected crystalline networks in fibers, tablets and prisms respectively. No bio-made crystallographic face bounds the biocrystal. Dislocations are virtually absent whereas microtwinning may be occasionnally abundant (Fig. 1). Crystal structure coherency length and crystallization directions may be tracked by such growth microtwinning. Inside the granules, high-resolution TEM shows a nanometric vermicular porosity, elastic distorsions and point defects (Fig. 2). This suggests intimate organo-mineral interaction up to the atomic scale. Amorphous granules may coat nacre tablets and prisms [1], and they act as Ca-providers for biocrystal growth within an encapsulated, extending network of fused granules.

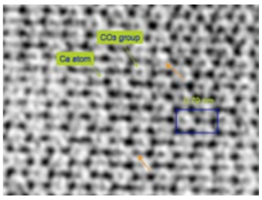

Figure 1: TEM view of fused granules with microtwins inside
Figure 2: HRTEM [001] view of bio aragonite with atomic defects

These nanometric scale observations made on a significant number of mollusk species support the concept of ‘moulded’ crystallisation from an amorphous and soft precursor [2], and they challenge the mesocrystal formation concept [3].

[1] Baronnet *et al.* (2008) *Min. Mag.* **72**, 539–548. [2] Addadi *et al.* (2006) *Chem. Eur. J.* **12**, 981–987. [3] Cölfen & Antonietti (2008) *Mesocrystals & Non Classical Crystallization*, Wiley & Sons Ltd, 276p.