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Société Française de Minéralogie et de Cristallographie

PRIX HAÛY-LACROIX 2007

The Prix Haüy-Lacroix recognizes a young scientist for the quality of his or her PhD research in the fields of mineralogy, geochemistry, petrology, or material science. This year, it was awarded jointly to Anne Verlaguet and Emmanuel Gardés during the SFMC 2007 general assembly on 12 June 2007, in Paris.



Anne Verlaguet obtained her PhD from the École Normale Supérieure (Paris) with a thesis entitled "Metamorphic Fluids and Mass Transfer: Experimental Approach and Study of HP-LT Veins from Vanoise (French Alps)." Bruno Goffé and Fabrice Brunet were her advisors.

Metamorphic veins are considered as the traces of fluid paths produced by dehydration reactions. However, no consensus exists on the mechanisms of vein formation. Do they result from external fluids (open system) or from in situ fluid–rock reactions (closed system)? Moreover, because of its low solubility, Al is generally considered as immobile, but this assumption is in contradiction to the ubiquitous occurrence of Al-minerals in veins. Anne Verlaguet's work combined a study of aluminous metamorphic rocks with an experimental study (tube-in-tube setup) and included modeling of fluid–mineral reactions.

In karstic metabauxites from Vanoise (French Alps), several generations of veins with distinct Al-bearing minerals formed during fluid–rock dehydration reactions (13–16% of rock volume) without external fluid input. Mass transfer was driven by aqueous species diffusion in the pore fluid or along mineral grain boundaries. In the rock volume between two neighbouring veins, the major elements (Al, Si, Fe, Mg, Li) are evenly distributed (determined using laser induced breakdown spectroscopy). The absence of diffusion profiles suggests that the characteristic elemental-diffusion length is greater than or equal to half the distance between the two veins, in agreement with characteristic diffusion times calculated from both grain boundary and pore fluid diffusion coefficients. Two types of veins occur: (1) veins synchronous with metamorphic reactions, with a mineral content related to the segregation of by-products, and (2) veins composed of minerals formed independently of reactions. Pressure-solution mechanisms in high-stress zones can drive preferential dissolution of minerals with a high molar volume. Crystallization morphologies in the veins and rock suggest that the nucleation sites and the energies of fluid–mineral interfaces can potentially drive selective transfer towards the veins. Regular vein spacing is controlled by the mechanical properties and dehydration reactions, while the width of veins depends on rock chemistry. This illustrates a relationship between mass transfer and rock deformation.

A large amount of Al is removed from the rock during metamorphic processes. Thus mass balance calculations considering Al as immobile must be used with caution. Experiments show that Al preferentially forms secondary minerals during fluid–mineral equilibration, due to its

low solubility relative to other elements. However, the calculated amount of precipitated Al-minerals, in response to P , T , or stress variations (SUPCRT92 modeling), is insufficient to explain the observed abundance of Al-minerals in veins. In contrast, the crystallization of Al-rich minerals resulting from the incongruent dissolution of aluminous minerals cannot be neglected in experimental studies that aim at determining mineral solubility.

Verlaguet A, Brunet F, Goffé B, Murphy WM (2006) Experimental study and modeling of fluid reaction paths in the quartz–kyanite±muscovite–water system at 0.7 GPa in the 350–550°C range: Implications for Al selective transfer during metamorphism. *Geochimica et Cosmochimica Acta* 70: 1772–1788



Emmanuel Gardés receiving the Prix Haüy-Lacroix from Catherine Mével, SFMC president, at the 2007 general assembly in Paris (Institut de Minéralogie et Physique des Milieux Condensés)

Emmanuel Gardés obtained his PhD from Université Paul Sabatier (Toulouse) at the Laboratoire des Mécanismes et Transferts en Géologie, with a thesis entitled "Diffusion of Lead in Monazite." Jean-Marc Montel and Olivier Jaoul were his advisors.

A knowledge of Pb diffusivity is necessary for understanding U-Th-Pb age anomalies of monazite. Atomic diffusion in minerals is usually slow. Thus, only submicrometric lengths of diffusion are commonly obtained from experiments. These low concentration profiles can only be measured using techniques with a spatial resolution of tens of nanometers,

such as Rutherford backscattering spectrometry or SIMS. TEM with a focused ion beam (FIB) sample preparation technique can be used. FIB is seen as an SEM where the electron gun is replaced by a Ga-ion gun (e.g. Wirth 2004, *European Journal of Mineralogy* 16: 863–876). A secondary electron detector allows one to view the sample surface and therefore to focus on the area of interest. As Ga ions are much heavier than electrons, FIB is used for sample surfacing at the nanometer scale and to extract electron-transparent foils from the surface. For its TEM use, a FIB foil is typically several micrometers wide and 100 nm thick; it is mounted with its largest face lying on the TEM grid. EDX spectrometry allows chemical analysis over the foil. As foils have constant thicknesses, changes in EDX signals are due only to chemical variations. This feature allows chemical mapping and especially diffusion profile measurements.

Experimental measurements of Pb diffusivity were done on a thin epitaxial film of $\text{Nd}_{0.66}\text{Pb}_{0.17}\text{Th}_{0.17}\text{PO}_4$ deposited on a synthetic NdPO_4 monocrystal (room pressure, 1200°–1500°C, 1 hour to 1 month). The expected $\text{Pb}^{2+} + \text{Th}^{4+} \leftrightarrow 2 \text{Nd}^{3+}$ exchange was observed by analyzing the species across the interdiffusion zone. Commonly, only the shape of the concentration profile is necessary. If the chemical composition variation over the sample remains low, the EDX signal is considered proportional to concentration. Thus, the EDX signals were not converted into concentrations, and diffusivities were determined by modeling the raw EDX signals with the solution of the diffusion equation. In the study of $\text{Pb}^{2+} \leftrightarrow \text{Ca}^{2+}$ interdiffusion in monazite, the exchange was performed between a thin film of $\text{Nd}_{0.70}\text{Pb}_{0.15}\text{Th}_{0.15}\text{PO}_4$ and a synthetic $\text{Nd}_{0.70}\text{Ca}_{0.15}\text{Th}_{0.15}\text{PO}_4$ polycrystal. FIB foils, ~15 μm long, were cut in the center of bigger grains (>20 μm), thus excluding grain boundaries and their contribution to diffusion profiles. In this case, the exact location of the working area on the surface of the sample is an asset. Therefore, polycrystals can be used for determining bulk diffusion coefficients, and this is particularly valuable when the growth of monocrystals with a specific composition is not possible. The main limitation of the technique is that isotopic diffusion profiles cannot be analyzed by EDX. In addition, for low concentrations, counting can be greatly improved if a microscope equipped with a field emission gun (FEG) is used. Then, TEM coupled to FIB sample preparation is a new and powerful tool for investigating submicrometric diffusion profiles.

Gardés E, Jaoul O, Montel J-M, Seydoux-Guillaume A-M, Wirth R (2006) Pb diffusion in monazite: An experimental study of $\text{Pb}^{2+} + \text{Th}^{4+} \leftrightarrow 2\text{Nd}^{3+}$ interdiffusion. *Geochimica et Cosmochimica Acta* 70: 2325–2336