Subject offered for a contract starting October 2017

SUBJECT TITTLE:

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Financing: Doctoral contract without teaching assignment

Presentation of the subject: (1 or 2 pages)

Chloride is the main ion in crustal and sedimentary fluids but is rarely used as geochemical tracer because it is believed that it is not or weakly modified by geochemical processes and consequently is refered as “non-reactive”. This naive scheme through which chloride variations are the consequences of other ions variations is no more acceptable when attention is given to chlorine stable isotopes ($^{37}Cl/^{35}Cl$). This isotopic tool reveals that chlorine isotopes get fractionated by numerous processes occurring in pore fluids such as diffusion, salt precipitation, gravitation … Yet few numerical constraints are available but set the start of a basis for numerical simulations of fluid transport in porous media. These are already used to reveal some stages of the history of fluid movements in porous reservoirs (See works by Eggenkamp, Godon, Lavastre, Giunta, Bernachot, Stash-Shouakar, Woulé-Ebongué, …).

In pore fluids of accretionary prism of the Nankai subduction zone, sampled by ODP Legs 131, 190 and 322, huge and enigmatic variations of chlorides $^{37}Cl/^{35}Cl$ are recorded (from 0 to -8 ‰). Until now the only proposed model (Ransom et al., 1995, Spivack et al., 2002 ; Wei et al., 2008), demands the sequestration of ^{37}Cl into alteration minerals. This model also predicts the outgassing of ^{37}Cl enriched volatiles by arc volcanoes. These two needs are in net contradiction to recent observations (Sharp et al., 2010 ; Rizzo et al., 2013; Li et al., 2015 ; Sharp and Barnes, 2008 ; Bonifacie et al., 2007 et 2008). Alternatively, the ion filtration, through which such ^{37}Cl depleted fluids could be formed, has been rejected on the basis of analog experiments that have never been published (Campbell, 1985 ; Haydon, 1983) or were realized in conditions very far from those of these pore fluids (Hanshaw and Coplen, 1973) and therefore are not deciding arguments.

The issue of ionic filtration is not limited to this academic/fundamental problem : since the 60’s, when the studies of pore fluids of oil and gas reservoirs started to display chemical variations, ion filtration has always been invoked as an essential process which determine the evolution of chemical

composition of fluids due to fluid movements in porous media (Oil and gas reservoirs, geological storage of CO_2, H_2, CH_4, hydrocarbons, …) and during Oil and gas shale extraction. Although so important, the modeling of ion filtration is reduced to rare attempts because of the lack of numerical contraints. These are missing for experimental reasons. Experiments are systematically hampered by the reactivity of chlorides which considerably alter the experimental means for long term runs.

The work will focuse on:

1) Analyzing the $\delta^{37}Cl$ of pore fluids in compacting sediments. Targets are Leg 322 (Nankai fore front, coll. C. Destrigneville, GET Toulouse), Leg 334 (Costa Rica Seismogenesis Project, Coll. M. Torres, Oregon State University, USA), and Leg 366 (Mariana Mud Volcano, Coll O. Sissmann, IFPen). In these compacting situations, the decrease of porosity sets a difference between the velocity of the fluid and that of the solid which must be the engine of some ion filtration.
2) Comparing these values to concentrations of other components of the fluids which might be affected by ion filtration (Na^+, H^2O, $^{18}O/^{16}O$, …)
3) Correlating gradients of concentrations with permeability barrier (clay with low permeabilities) which have the potential of producing ion filtration.
4) Building model of mobility of fluids in compacting porous media. Two ways are planned :
   - Box model from conservation equations written for water molecules and chlorides (cf Henry et Bourlange 2004)
   - Finite difference model of transport equation in porous media (cf Berner, 1980; Hutchison, 1985; Rabouille et Gaillard, 1991)

This approach will afford numerical values for the minimal isotopic fractionation of chlorine isotopes during ion filtration. Indeed other processes occurring in porous media, mainly diffusion, mainly homogenize isotopic gradients and will have tendency to reduce the isotope fractionations produced by ion filtration. (see Lavastre, Giunta, Bernachot)

Références

Bernachot et al., Submitted to Chemical geology 2016
Berner R. Early diagenesis, A theoritical approach, in Geochemistry 241pp
Bonifacie et al. Earth and Planetary Science Letters 260 (2007a) 10–22
Bonifacie et al. Chemical Geology 242 (2007b) 187–201
Campbell, 1985, Master of Science thesis Univ. Arizona unpub Manuscript
Eggenkamp H. et al., Chemical Geology 433 (2016) 46–56
Giunta T. et al., Submitted to Nature Géosciences 2017
Hanshaw et Coplen, 1973, Geochimica et Cosmochimica Acta, 1973, 37, 2311 to 2327
Haydon, 1983, PhD thesis University of Illinois at Urbana-Champaign
Henry et Bourlange, Earth and Planetary Science Letters 219 (2004) 129-145
Hutchison, Geophys. J. R. astr. Soc. (1985) 82, 439-459
Lavastre et al. , Geochimica et Cosmochimica Acta, Vol. 69, No. 21, pp. 4949–4961, 2005
Li et al, Earth andPlanetaryScienceLetters413(2015)101–110

Phillips and Bentley Geochimica et Cosmochimica Acta 51 (1987) 683-695
Rabouille et Gaillard, JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 96, 2761-2776, 1991
Ransom et al., Geology; August 1995; v. 23; no. 8; p. 715–718
Rizzo et al., Earth andPlanetaryScienceLetters371-372(2013)134–142
Sharp and Barnes Earth and Planetary Science Letters 274 (2008) 531–534
Sharp et al., Geochimica et Cosmochimica Acta 74 (2010) 264–273
Spivack et al., GEOPHYSICAL RESEARCH LETTERS, 29, NO. 14, 1661, 2002
Wei et al, Earth and Planetary Science Letters 266 (2008) 90–104

Planned interactions

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