

Introduction

Geochemistry of crustal fluids: an Andalusian perspective

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1. Introduction

This special issue brings together manuscripts presented or inspired by the third European Research Conference on the Geochemistry of Crustal Fluids, held in Granada, Spain in December 2000. The goal of this meeting was to bring together scientists and students that work on small confined systems with those focusing on global scale assessments and modelling. There were 23 invited speakers at the meeting and 80 other participants, of whom 40 were invited young European Scientists and seven were invited from the former Eastern Bloc Countries in Europe. Oral presentations were held during the morning and early evening; but poster sessions during the late evening (Figs. 1 and 2). Fortunately, ample free time was available to discuss the latest advances in crustal fluid chemistry at the Flamenco caves (Fig. 3), on the ski slopes (Figs. 4–6), at the outdoor bar high up in the Sierra Nevada (Figs. 7 and 8) and in the Alhambra (Fig. 9). The conference banquet will be long remembered for the singing (Figs. 10–13) and dancing, which lasted until early morning.

This volume is intended to reflect the breadth of the subjects. We are proud and impressed by the quality and scope of the 22 manuscripts presented in this volume. These manuscripts fall into six broad themes: (1) geochemical cycles; (2) weathering rates in soils; (3) river studies; (4) the studies of springs, geothermal wells and fluid inclusions; (5) low temperature experiments, mineral surface structures and chemistry; (6) trace elements in natural waters and contamination. A brief summary of these themes is given below.

1.1. Geochemical cycles

Much effort has been dedicated towards the short- and long-term carbon cycle during the last decade. In the first paper of this issue, Mackenzie et al. (2002) define the role of anthropogenic nitrogen and phosphorus in controlling the global carbon cycle since the year 1850 with projections to the year 2035. Tranter et al. (2002) describe the glacial bicarbonate, sulphate and base cation fluxes during the last glacial cycle, and their effect on atmospheric CO₂. They conclude that the change in atmospheric CO₂ concentration during the last glacial cycle due to perturbations in glacial solute fluxes is insignificant, less than 1 ppm. Dunk et al. (2002) present a new assessment of the pre-anthropogenic uranium budget for the Holocene

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Fig. 1. Posters are fun. Fred Mackenzie and Michel Meybeck by the posters.

Ocean where the dominant source was river runoff and the direct discharge of groundwater could represent a significant additional input.

1.2. Weathering rates in soils

The chemical weathering rates of minerals in soils play a major role in a number of geochemical processes, including soil nutrient cycling, neutralisation

of acid precipitation and long-term atmospheric CO₂ fixation. In this volume, White (2002) introduces an integrated approach for determining mineral weathering rates based on regolith solid and solute elemental gradients. This approach is applied to biotite weathering in Saprolites. The biotite-weathering rate in this study was three to six orders of magnitude slower than corresponding experimentally measured rates. Hudson (2002) measured experimentally the far



Fig. 2. The hard core by the posters. Mark Hudson, Björn Jamtweit, Eric Oelkers and Susan Brantley.



Fig. 3. Art White in full swing. Flamingo at its best! From left to right: Laurent Charley, Susan Stipp, Mark Hudson, Ulla Hofmann, Albert Galy and Céline Dessert admiring the invention of the new step: “flamingo-west”.

from equilibrium dissolution rate of different mineral size fractions from the B-horizon of a granitic podzol. The different size fractions were mineralogically and chemically similar. The smallest grain size was the most important for element release into the soil. Gordon and Brady (2002) measured the in situ long-term basaltic glass dissolution in the unsaturated zone. Measured rates represent weathering over 3000 years and were substantially lower than glass dissolution rates measured in the laboratory over much shorter time spans.

1.3. River studies

The evolution of seawater pH is of particular interest since it is sensitive to changes in past atmos-

pheric CO₂ and hence global climate. Boron isotopes have been used as a proxy for past ocean pH. Lemarchand et al. (2002) present the systematics of boron isotopic composition of the world’s main rivers. They show that the oceanic boron cycle is mainly controlled by the boron continental river discharge and the boron uptake from the oceans during the low temperature alteration of oceanic crust. Although, as illustrated by Lemarchand et al. (2002) for the case of boron, dissolved chemical fluxes to the oceans, carried by the world rivers are relatively well defined. Much less is known, however, about the flux of colloids and adsorbed chemical species to suspended matter in rivers and their sorption/desorption once in the estuary. Pokrovsky and Schott (2002) measured the iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries in Northwestern Russia. Samples were filtered in the field through filters of progressively decreasing pore size. Their study revealed two pools of colloids, organic and Fe-rich particles. Iron concentration decreased gradually upon filtration from 5 μm to 1 kD whereas the major part of organic carbon was concentrated in the smallest fraction, 1–10 kD. Trace elements are apparently transported as coprecipitates with iron oxy(hydr)oxides, rather than adsorbed on the iron oxy(hydr)oxide surface. Some elements are scavenged by iron during coagulation of Fe-hydroxide colloids in the Russian estuaries. Gislason et al. (2002) measured the dissolved fluxes of about 50 elements and chemical species and the stable isotopes of H, O, C and S and ¹⁴C associated with the 1996 eruption and flood within the Vatnajökull glacier, Iceland. About half of the measured total magmatic carbon flood flux from the 1996 Vatnajökull eruption will be added to the long-term CO₂ budget of the oceans and the atmosphere. The other half will eventually precipitate in the ocean as carbonates with released Ca and Mg. Subglacial eruptions affecting the surface layer of the ocean where either Mn, Fe, Si or Cu are rate-determining for the growth of oceanic biomass have the potential for a transient net CO₂ removal from the ocean and the atmosphere.

1.4. Springs, geothermal wells and fluid inclusions

A major application of studying water chemistry in active volcanic regions is the possibility of pre-



Fig. 4. Skiing in “the real Sierra Nevada”. From left to right: Vala Ragnarsdóttir, Oleg Pokrovsky, Jacques Schott and Jerome Gaillardet.

dicting the timing of future eruptions. [Martin-Del Pozzo et al. \(2002\)](#) defined the magmatic interactions with spring water at Popocatepetl Volcano, Mexico, during the volcanically active period 1994–2000. There was a significant variation in the concentration of the major anions in the spring waters preceding eruptions in Popocatepetl during the 1994–2000, and

boron variation was detected before the largest volcanic events.

Understanding the flow of fluids in fault zones provides insight about the development of earthquake mechanism models. [Pili et al. \(2002\)](#) used carbon–oxygen isotope and trace elements to put constraints on how fluids percolate into faulted limestone from



Fig. 5. The “professionals” from left to right: Ingvi Gunnarsson, Ingunn Thorbergdóttir, Art White, Eydís Eiríksdóttir, Anne Hermans and Paul Frogner.

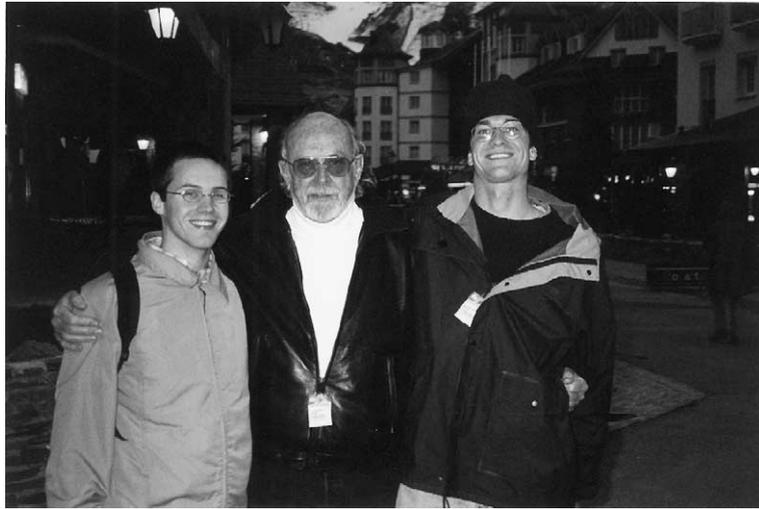


Fig. 6. The master of elegance on the ski slopes, Hal Helgeson, Douglas LaRowe (left) and Jeff Dick (right). The question remains: Where is the first aid kit?

the San Andreas Fault system. In contrast to what is commonly believed, fluid flow is not restricted to veins or deformation zones. Significant fluid flow took place in the host rocks near fault zones. Hence, the nature of the rocks in fault zones must be considered to accurately quantify the role of fluids in seismic cycles.

Knowledge of the composition and speciation of geothermal fluids is a prerequisite for understanding their origin and evolution, the formation of hydrothermal ore deposits and the redox conditions in the vicinity of future nuclear waste repositories. With the aid of data on the partial pressure of various gases and the activity of dissolved species from high



Fig. 7. Beer has never tasted better! From left to right: Ulla Hofmann, Susan Stipp, Jacques Shott, Vala Ragnarsdóttir, Albert Galy, Mark Hodson, Anne Hermans and Ingvi Gunnarsson.



Fig. 8. The chairman's thought: "Looks like this conference is going to be a success". Sigurdur (Sigg) Gislason and Malfridur (Malla) Kristiansen.

temperature geothermal wells in Iceland, [Stefánsson and Arnórsson \(2002\)](#) defined the redox conditions in the geothermal fluids. Overall, equilibrium among redox species was not reached for dilute geothermal fluids, whereas saline geothermal fluids were closer to overall redox equilibrium.

Regional metamorphism in conjunction with a high fluid flow could lead to the formation of ore deposits. [Guedes et al. \(2002\)](#) used fluid inclusions to study the evolution of fluids associated with metasedimentary sequences from Chaves, North Portugal. The study indicated multiple fluid circulation events with a



Fig. 9. "The sultans of Alhambra", Jacques Schott and Bill Davidson.



Fig. 10. Toast at the banquet. Around the table from left: Paul Frogner, Stefán Arnórsson, Terry Seward, Duncan Harris, Carla M. Koretsky, Johnson Haas, Suvasis Dixit and Andri Stefánsson.

variety of compositions within the C–H–O–N–salt system.

1.5. Low temperature experiments, mineral surface structures and chemistry

The three minerals focused on in articles found in this chapter, calcite, iron hydroxide and pyrite, are particularly significant for natural surface waters:

calcite, because of its abundance, rapid dissolution rate and fixation of CO₂; iron hydroxide because of its enormous specific surface area and its ability to scavenge trace elements from surface waters; and pyrite because of its oxidative dissolution and ensuing acidification of surface waters.

Calcite dissolution at acid conditions plays a major role in a number of natural and industrial processes including acid fracturing in carbonate petroleum re-



Fig. 11. “O sole mio”, The Italian delegation at its best, from left to right: Lisa Pierotti, Maura Pellegrini, Francesca Spadaro, Chiara Giolito and Sabrina Pastorelli.



Fig. 12. “All you need is love, da, da, radadaaaa...” The British–Irish number at the banquet. Martin Tranter, Bill Davidson and Michael Duane.

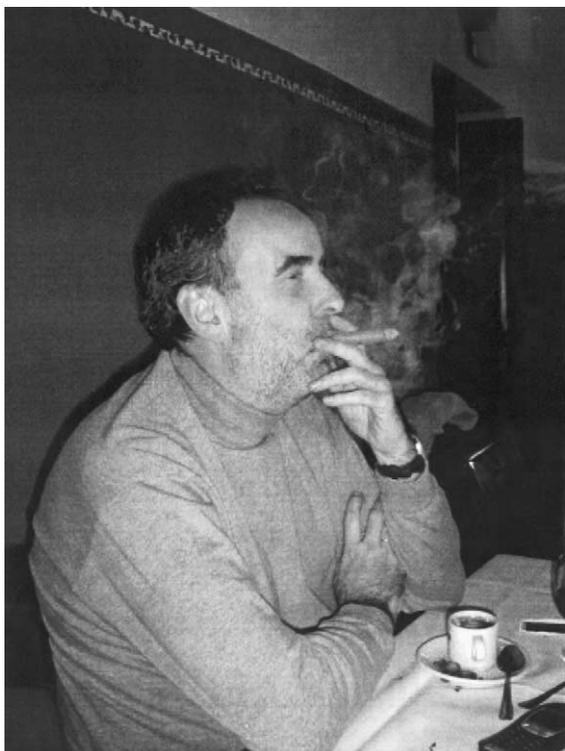


Fig. 13. “How did he do it?” The chairman to come, Jordi Bruno in deep thought.

reservoirs, the destruction of building facades by acid rain, and the neutralisation of acid mine waste waters. [Alkattan et al. \(2002\)](#) experimentally measured calcite dissolution rates at acidic conditions and 25 °C in the presence of NaPO_3 and MgCl_2 . Magnesium was found to have no effect, but phosphate was found to inhibit calcite dissolution at acidic pH.

[Charlet et al. \(2002\)](#) studied by contact mode atomic force microscopy (AFM) the in situ natural attenuation of trichlorethene (TCE), As, Hg, linked to the heterogeneous oxidation of Fe(II). Hydrous ferric oxide colloids formed in strictly anoxic conditions upon the oxidation of Fe^{2+} ions adsorbed on a phlogopite crystal. The reduction of the Hg, As and TCE appears to be driven by the high reactivity of adsorbed Fe(II). This finding is of environmental importance since these three priority pollutants are thus reductively transformed into volatile, an immobile and a biodegradable species, respectively.

[Stipp et al. \(2002\)](#) studied the behaviour of Fe-oxides relevant to contaminant uptake in the environment with the aid of atomic force microscopy, X-ray powder diffraction with Rietveld refinement, time of flight secondary ion mass spectroscopy and transmission electron spectroscopy. Adsorption isotherms for Ni^{2+} uptake on the Fe-oxides were all similar, increasing at high pH. Desorption behaviour was also similar, but one third or more of the Ni^{2+} failed to

return to solution, leading to the conclusion that Ni^{2+} must be incorporated onto or into the solids. Geochemical speciation models that fail to account for contaminant uptake in solid solutions within major phases or as thin coatings or entrained crystals of uncommon phases risk underestimating contaminant retardation or immobilisation.

Doménech et al. (2002a,b) experimentally determined the oxidative dissolution rate of pyrite sludge from the Aznalcóllar mine in Southwest Spain, at 22 °C and pH 2.5–4.7. Pyrite and chalcopyrite dissolved at similar rates, whereas sphalerite dissolved faster. They propose that the rate-limiting step is the surface oxidation of sulphide to sulphate after the adsorption of O_2 onto pyrite surface.

1.6. Trace elements in natural waters and contamination

One of the major motivations for studying the geochemistry of near surface fluids is to determine the fate and transport of toxic and radioactive waste products. There are four insightful examples of such efforts in this volume (Doménech et al., 2002a,b; Bruno et al., 2002; Pérez del Villar et al., 2002; Antunes et al., 2002).

On 25 April 1998, the tailing dam of the Aznalcóllar mine, 25 km NW of Sevilla, Spain, collapsed and the valleys of the Agrio and Guadiamar rivers were flooded with 4 hm³ of sulphide sludge. The sludge was mostly pyrite, with a minor amount of sphalerite, galena, chalcopyrite, arsenopyrite and sulphosalts. The oxidation of the sludge resulted in acid drainage and metal pollution of the river and groundwater. The sludge weathering and mobility of contaminants in the soil affected by the Aznalcóllar mining accident were studied by column experiments by Doménech et al. (2002a,b). The pH of the water fell to 2 after 260 days and the concentrations of Zn, Cd and Co in the leachates matched the expected values from flow-through experiments at atmospheric oxygen pressure. At the low pH jarosite formed, resulting in depletion of As, Pb, Sb and probably Tl.

Natural analogue studies have become an integral part of the safety assessment of nuclear waste repositories. These studies have made it possible to test the conceptual geochemical models, the associated thermodynamic database and the required numerical

models to describe radionuclide migration under repository conditions. Bruno et al. (2002) studied the applicability and limitations of thermodynamic geochemical models simulating trace element behaviour in natural waters. The lessons learned from the natural analogue studies of Pacos de Caldas, Brasil, Cigar Lake, Canada, Maqarin, Jordan, El Berrocal, Spain, Oklo, Gabon and Palmottu, Finland are discussed in the paper.

Along these lines, Pérez del Villar et al. (2002) described the uranium ore from “Mina Fe” Salamanca, Spain and used it as a natural analogue of radioactive spent fuel. The physico-chemical conditions of the oxidised zone are not relevant to disposal conditions. In the transition zone, two main geochemical processes take place: (i) the coffinitisation of pitchblende, which may be an important process for the stability of spent fuel under reducing conditions, and (ii) the coprecipitation of the Fe(III) and U(VI) as oxyhydroxide. The physico-chemical conditions that prevail below 50 m depth should be sufficient to stabilise a spent nuclear fuel repository, in the same way as they have been able to preserve the 34-my-old uranium deposits of the “Mina Fe”.

In Central Portugal there are several metal deposits, which have been exploited and then left abandoned. At Segura, Central Portugal, there are Sn–W and Ba–Pb–Zn deposits that were exploited until 1959, as described by Antunes et al. (2002). The tailings and rejected ore were not covered by vegetation. Hence, acid waters were formed with a relatively high concentration of metals such as As, Fe and Mn and soils are contaminated with Sn, B, As and Ba.

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