

Grain-boundary fluids, chemical transport, and rheology: An Alpine perspective and resulting questions

JANE SELVERSTONE

Department of Earth & Planetary Sciences, University of New Mexico, Albuquerque, NM, USA (selver@unm.edu)

Experimental studies on wetting behavior of fluids have profound implications for understanding a variety of chemical and physical processes during synchronous metamorphism and deformation. The difficulty comes in determining how field and petrographic observations relate to the experimental data. Examples from the Eastern Alps will be used to document scales of fluid communication during metamorphism, to estimate wetting behavior of the fluids, and to explore effects on rock rheology: (1) Mineral and stable isotopic compositions in banded eclogites are homogeneous parallel to foliation but heterogeneous across foliation. Sharp interfaces rule out cross-foliation diffusion or fluid flow on a mm scale. Any interconnected porosity at high P was thus confined to layer-parallel networks. (2) Diffusive mass transfer during deformation of clast-bearing micaceous quartzites required an inter-connected fluid phase during amphibolite-facies shearing, but was ultimately self limiting. Rheologic cycling resulted from feedback effects between mass transfer and changes in deformation mechanisms. (3) Schists in the same shear zone contain carbonic fluid inclusions in graphitic layers vs. H₂O inclusions in nongraphitic layers. Strain was accommodated by repeated fracturing in graphitic layers and by crystal plasticity in nongraphitic horizons. Non-wetting carbonic fluids in graphitic schists experienced significant volume expansion during decompression, causing fracturing (and possible seismogenic faulting). (4) Preliminary rock-deformation experiments confirm the role of CO₂ in promoting high-T embrittlement of quartz-rich rocks, and also show development of rheologic stratification in samples deformed in the presence of immiscible H₂O-CO₂ fluids.

These studies show that variations in fluid wetting behavior control both mass transfer and rock rheology. They also raise questions: How does deformation affect fluid wetting behavior? What role does fluid immiscibility play in controlling rheology during deformation? What data are needed from natural samples to infer paleo wetting behavior? Does wetting behavior play a role in the earthquake cycle? Closer collaboration between field and experimental scientists is needed to address these questions.

Garnet morphology and the kinetics of deep crustal reactions

D.E. WILBUR^{1,2} AND J.J. AGUE¹

¹Department of Geology and Geophysics, Yale University, P.O. Box 208109, New Haven, CT 06520-8109 USA (jay.ague@yale.edu)

²Brinkerhoff Environmental Services, Inc, 1913 Atlantic Ave., Manasquan, NJ 08736 USA (dwilbur@brinkenv.com)

The kinetics of deep crustal reactions have important implications for rates of fluid release and the impact of fluids on rock strength and seismic hazard. We focus on growth textures preserved in garnets from two rock units within the Acadian Orange-Milford Belt, CT: meta-ultramafic rocks found in the Maltby Lakes Metavolcanics (MLM) and metapelitic rocks of the Wepawaug Schist (WepS).

And-Grs-Uv garnets of the MLM rocks nucleated on relic spinels and have rounded, "petal-like" shapes. Garnet to Kyanite zone garnets in graphitic rocks of the WepS contain anhedral or "star-shaped" cores with relatively few inclusions. The cores abruptly give way to sub- to euhedral rims rich in inclusions of graphite and Fe-Ti oxides. Cores have larger Ca, Mn, and Fe/Mg than rims. Core-rim boundaries are marked by agglomerations of graphite. Similar features in graphitic metapelitic rocks elsewhere define "textural sector zonation" (TSZ; Rice and Mitchell, 1991). Garnets with TSZ are found only in graphitic WepS rocks, ruling out graphite precipitation events at core-rim transitions. Instead, the organic matter was present prior to garnet nucleation, but it was excluded from the garnet cores as they grew.

The garnet morphologies imply rapid growth and fluid release far from equilibrium at large delta G of reaction. Morphology diagrams (e.g., Xiao et al., 1988) suggest that the petal-like shapes of the MLM garnets represent the fastest growth rates farthest from equilibrium. The WepS garnet cores represent somewhat slower, but still highly overstepped, growth that was followed by slower, more euhedral rim growth. We suggest that rapid growth coincided with rapid regional heating, consistent with recent geochronology (Lancaster et al., 2005).

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Mineral dissolution kinetics at grain boundaries

A. LUTTGE^{1,2}

¹Department of Earth Science, Rice University, Houston, Texas, USA (aluttge@rice.edu)

²Center for Biological and Environmental Nanotechnology (CBEN), Rice University, Houston, Texas, USA

Mass transport of dissolved components in the shallow subsurface may often occur via a dissolution-precipitation mechanism, a process for which two decades of experimental study have provided substantial support. However, these studies were conducted in autoclaves at elevated temperatures and pressures. Direct observations of the mineral surfaces that constitute these reacting systems were prohibited, and thus kinetic mechanisms were not understood in any detail.

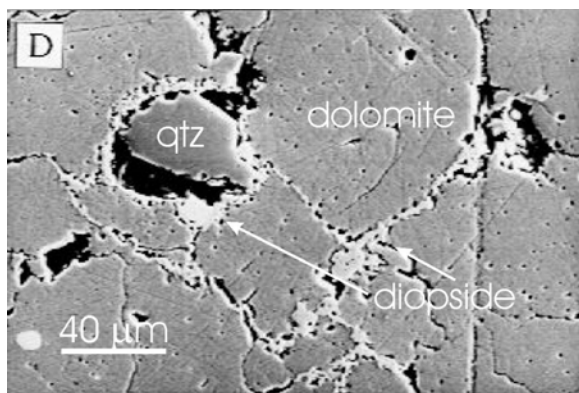


Figure 1: SEM photomicrograph of a dolomite quartz rock reacting to form dioside and CO₂ at 500 MPa and 680 °C (Luttge, 1995).

Recently, several researchers, e.g., Putnis (2004) and Baumgartner (2004), have revived interest in this research topic. While revisiting the mechanistic concepts they have highlighted in particular the importance of coupled mineral dissolution-precipitation kinetics.

In this context, our studies of crystal dissolution kinetics at lower temperatures (10 - 180°C) may help to shed some more light on this important problem. We employ a combination of direct observational techniques, i.e., atomic force microscopy (AFM) and vertical scanning interferometry (VSI) and computer simulations. Our research has led to a new model that emphasizes the importance of full incorporation of the three-dimensional crystal lattice into a fundamental kinetic treatment. Our stochastic approach is based on parameterized Monte Carlo techniques. *Ab initio/DFT* calculations are used for the parameterization.

Grain and phase boundaries and viscoelastic mechanical response

REID F. COOPER

Dept. of Geological Sciences, Brown University, Providence, RI, 02912-1846, USA (reid_cooper@brown.edu)

The phenomenologies of creep and of seismic-frequency wave attenuation are intimately associated with the spatial distribution and structure & chemistry of grain and (solid-state) phase boundaries. My students and I pursue experimental research to quantify the relationships; the studies emphasize (i) state-variable analysis/description of dislocation-effected plasticity, (ii) phase- and grain-boundary effects on wave attenuation, and (iii) plastic-strain-effected phase separation in polyphase aggregates.

(i) Stress-relaxation experiments suggest that the dislocation rheology can be predicted in a strain-insensitive manner through use of a *single* microstructural state variable. It is the distribution of low-angle grain boundaries that corresponds to this state variable, and thus the physics of deformation is dependent on dislocation dynamics within those boundaries.

(ii) The power-law Q^{-1} v. f spectrum (“attenuation band”) associated with the damping of seismic waves can result from a *single* loss mechanism having a non-exponential relaxation—specifically, one associated with chemical diffusion to relieve gradients in grain-boundary traction. Experiments scrutinizing the small anelastic strains involved in attenuation suggest that a threshold phenomenon related to electrochemical segregation to grain boundaries may be prevalent. Solid-state phase boundaries have been demonstrated as particularly strong mechanical absorbers, with implications, e.g., that hydrous-phase breakdown reactions in nature could produce rocks that *combine* high stiffness (fast velocities) with high attenuation.

(iii) Large-scale plastic strain in polyphase aggregates requires components of grain- and phase-boundary sliding. The relative sliding viscosities *must* result in solid-state phase separation (mineralogical layering) accompanying deformation. Discerning experimentally the scaling relationships could allow correlation of such natural structures with the thermodynamic conditions (σ, T) that produced them.

The energetics of grain/phase boundaries, modeled as arrays of lattice dislocations (for low-angle boundaries) or disclinations (for high-angle boundaries) are applied to understand the physical relationships uniting these observations.

Hem-switching, chemically induced grain boundary migration, and rocks

BRIAN EVANS

Dept. EAPS, 54-718, Mass. Inst. Tech., Cambridge MA 02139,
USA (brievans@mit.edu)

Based on observations of the microstructure of Bavarian granites, Voll (1960) described a process that he called *Wechselsäume*, i.e., hem-switching, in which mixing and unmixing could occur via intergrowth of two mineral phases. The geometry, microstructure and chemistry that he described are equivalent to those formed during chemically induced grain boundary migration, a process recognized nearly 20 years later during laboratory experiments in metals with (Yoon and Huppman 1979) and without partial melts (Hillert and Purdy, 1978) and, later still, in ceramics and minerals. In the laboratory, the process is favored under conditions where the distance of boundary migration is greater than that associated with lattice diffusion of the reactants. During solid-solution reactions, the kinetic driving force appears to be constrained by elastic coherency forces along the migrating interface. As boundaries migrate through the solvent phase, the solute concentrations incorporated in the zone are smaller than that of a homogeneous solid-solution.

In order to understand the kinetics and driving forces for this process we have been studying the solid solution of divalent cations into calcium carbonates. In bicrystals, the coherency strain hypothesis explains many, but not all, of the aspects of mixing (Hay and Evans, 1992). More recently, we conducted experiments in which calcite and dolomite at 800°C react to form high magnesian calcite. After an early induction period, grains of both high Mg-calcites and Ca-rich dolomites are nucleated and grow slowly. This growth is then followed by rapid replacement of the early nucleation products by more stoichiometric dolomites. Thus, the overall dolomitization reaction occurs by at least three elementary reactions: nucleation of reactive intermediates, growth of the metastable phases, and replacement by dolomites with thermodynamically optimized stoichiometry. Thus far, CIGM has been produced in the laboratory only in the carbonate system, but it seems likely that such a process is possible during the formation of solid solutions in any mineral phase, and that CIGM be a wide-spread natural process.

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A new thin film approach to study grain boundary transport in an incompatible matrix

R. DOHMEN

Institut für Geologie, Mineralogie und Geophysik, Ruhr-
Universität Bochum, Universitätsstr. 150, 44780 Bochum
(ralf.dohmen@rub.de)

Recently, Dohmen and Chakraborty [1] have developed a general kinetic model for an exchange reaction between two solids mediated by an "intergranular fluid phase". One application of the model is that it allows to evaluate the integrated transport properties of an intergranular fluid phase by modeling of the compositional profiles in the solid reactants. As a test of the model and as an alternative way to study grain boundary transport in e.g. metals, oxides or silicates, a new experimental setup was developed. The general idea is that single crystals (e.g. olivine) are deposited with inert polycrystalline thin films (e.g. ZrO₂) of defined geometry and chemistry, such that any exchange with the covered surface of the single crystal has to pass this inert layer.

Single crystals of San Carlos olivine (Fo₉₀) were deposited with 100 to 500 nm thick layers of ZrO₂ by Pulsed Laser deposition [2]. Two sets of diffusion experiments were performed with these samples: (1) Diffusion anneals in the temperature range 900 – 1100°C in which the samples have an additional olivine thin film with Fo₃₀ composition on top of the ZrO₂ layer. (2) Diffusion anneals at 1200°C, where olivine samples were packed into olivine powder with Fo₃₀ composition. The analyses of the final chemical zoning with either Rutherford Backscattering or Electron Microprobe show that in the lower temperature range (<1100°C) the ZrO₂-film is not any kinetic barrier for the exchange between the olivines. However, in the experiments at 1200°C (experimental set 2) we observe non-equilibrium phenomena partly related to the ZrO₂ film and partly related to the insufficient contact with the surrounding powder. According to [1] this reaction system is controlled by solid state + fluid diffusion. Further experiments (e.g. a time series) at these conditions are going to be performed and the analytical observations as well as a quantitative modeling of the chemical zonings will be presented at the meeting.

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Grain-boundary and intra-crystal dissolution-reprecipitation reactions in alkali feldspars

I. PARSONS¹ AND M.R. LEE²

¹Grant Institute of Earth Science, University of Edinburgh, UK (ian.parsons@ed.ac.uk)

²Centre for Geosciences, University of Glasgow, UK

Most alkali feldspars exhibit exsolution or replacement microtextures (perthite). Regular, μm -scale 'strain-controlled' perthites form by continuous processes involving only volume diffusion of Na^+ and K^+ (plus Ca^{2+} and coupled Al^{3+} in ternary feldspars) through an Al-Si-O framework which remains continuous (coherent). The different ionic radii of Na^+ and K^+ lead to elastic strain and exsolution lamellae adopt crystallographic orientations which minimize strain energy. Irregular, much coarser, discontinuous (incoherent) 'deuteric perthites' form by dissolution-reprecipitation 'unzipping' reactions driven by release of coherency strain. These affect entire >1 cm crystals without modification of crystal shapes.

In the Klokken intrusion layers of impermeable fine-grained syenite (feldspar bulk composition $\sim\text{Ab}_{60}\text{Or}_{40}$) are interleaved with layers of compositionally similar, permeable coarse grained syenite. Sub- μm cryptoperthites in the former have a 'braid' configuration which is modified by forces acting between adjacent crystals, so that the textures form a 'strain-map'. The textures coarsen to $\sim 20\mu\text{m}$ near crystal boundaries leading to 'pleated rims' in which Na- and K-rich volumes alternate on opposing crystal surfaces. The local change in bulk composition leads to change in the lamellar texture to parallel films with edge dislocations (semi-coherent). The dislocations allow ingress of water into crystals and local development of patch perthites.

Patch perthites (up to $250\mu\text{m}$) dominate in the coarse syenites although relics of braid microtexture persist. TEM shows that individual patches are mosaics of incoherent subgrains which CL shows have well developed, 1-10s of μm oscillatory zoning at blue-UV wavelengths. Adjacent albite or microcline subgrains may display the same zoning pattern, with individual zones traceable over 100s of μm , implying dissolution in laterally extensive fluid films. Laser ICPMS shows that Ga, Rb, Sr, Ba, La, Eu, Pb and Cs partitioned isochemically in bulk from braid into Ab- and Or-rich patches, whereas Fe, Ti, Ni, La, Ce, Pr and Nd were lost from crystals during unzipping. After unzipping, Or-rich patches underwent a further phase of strain-controlled exsolution leading to straight lamellar cryptoperthites with dislocations. Solvus relationships show that this occurred at $\leq 350^\circ\text{C}$, implying that the deuteric fluids had ceased to play a role below this T .

Importance of Ar, He transport and partitioning in grain boundaries

ETHAN F. BAXTER

Department of Earth Sciences, Boston University, 685 Commonwealth Ave. Boston, MA 02215 (efb@bu.edu)

Analysis of noble gases, most notably Ar and He, in rocks and minerals are used in a variety of geological applications including geo- and thermochronology, tracing crustal recycling, and reconstructing Earth's degassing history. Interpretations of such data are effected by the manner in which the gases are partitioned between system phases (or reservoirs) and therefore reflect the noble gas content of the environment from which the samples were derived. Partitioning also effects the net rate by which the gases are transported in a given system. Mineral-mineral grain boundaries represent one reservoir common to all "dry" rocks into which noble gases may be partitioned and stored, and through which noble gases may be efficiently transported.

An experimental method has been developed for the measurement of grain boundary partition coefficients for noble gases. ^{37}Ar and ^4He are introduced into solid diopside composition glass samples via neutron irradiation. Samples are crystallized in sub-solidus conditions in a piston cylinder at 1350-1550 C and 2-3 GPa. Noble gases simultaneously equilibrate between the evolving crystal and grain boundary reservoirs. After equilibration, G.B. Ar and He is differentiated from that within the crystals by means of bulk step heating analysis. Results suggest an expected trend of decreasing bulk G.B. noble gas content with increasing grain size and yield a value of effective grain boundary surface partitioning, K_{surf} , in units of $(\text{mol Ar}/\text{m}^3 \text{ of solid})/(\text{mol Ar}/\text{m}^2 \text{ of GB})$ of $6.8 \times 10^3 - 2.4 \times 10^4 \text{ m}^{-1}$. Values for He are less well constrained but lie in a similar range.

These data suggest that grain boundaries constitute a significant, but not infinite, reservoir, and therefore bulk transport pathway, for noble gases in nominally dry systems (i.e. free of a fully wetting fluid phase). For example, this parameter may be used in a physical model of the local development of excess Ar (or He) (Baxter 2003) to help predict the amount of excess Ar (or He) that would be sequestered in the phases of a nominally dry system such as many ultra-high-pressure crustal settings or portions of the mantle. Also, partitioning and transport of noble gases into melts will be influenced initially by mineral-mineral grain boundaries where up to 30% of the bulk rock noble gas could potentially be stored before incipient melting.

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On the process of dihedral angle change

M.B. HOLNESS

Dept. Earth Sciences, University of Cambridge, Cambridge,
CB2 3EQ, UK. (marian@esc.cam.ac.uk)

Interstitial phases in igneous rocks commonly pseudomorph the residual porosity, with shapes inherited from melt-filled pores. The inherited angle at pore junctions may reflect either an impingement texture (e.g. Elliot *et al.*, 1997) or melt-present textural equilibrium. Since these are lower (median < 60°) than solid-state equilibrium values (~ 120°), such pseudomorphs are out of textural equilibrium. The solid-state texture will thus move towards one of larger dihedral angle. Interstitial clinopyroxene in cumulates from the Rum Layered Series shows variable approach to solid-state textural equilibrium from an initial inherited state. In contrast to the currently accepted model of dihedral angle change, which assumes an instantaneous establishment of the new angle at the pore corner with subsequent outwards propagation of the new surface curvature (Mullins, 1957), textural equilibration at pore corners actually occurs as a continuous process, with a gradual movement of the entire dihedral angle population towards the equilibrium final state. At any instant during this process, the static dihedral angle equation (Herring, 1951) does not hold.

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Quartz-H₂O dihedral angles and crystal misorientation

J.B. THOMAS¹, D.A. WARK¹, E.B. WATSON¹
AND Z. JIANG²

¹Dept. of Earth and Environmental Sciences, Rensselaer
Polytechnic Institute, Troy, NY, USA (thomaj2@rpi.edu)

²Dept. of Geology and Geophysics, Yale University, New
Haven, CT, USA

The physical and chemical properties of deep-seated rocks are strongly influenced by the presence and intergranular geometry of fluids. At equilibrium, the latter is strongly determined by solid-solid interfacial energies.

In order to better understand the role of interfacial energies in determining fluid topology, we developed a new experimental technique for characterizing the 3-D geometry of individual pores. The technique involves introduction of H₂O along synthetic grain boundaries produced in a piston-cylinder apparatus by juxtaposing polished quartz disks at high P and T. H₂O trapped along the interface forms lenticular pores during the experiments as the grains weld together to form a grain boundary. After the experiment, grain boundaries were separated to expose half of each fluid-filled pore on complementary disks. Two advantages of this technique are that the: (1) 3-D pore geometry can be directly measured using atomic force microscopy thus removing effects caused by random sectioning of pores, and (2) solid-solid interfacial energy can be controlled by varying the amount of crystal lattice misorientation (determined by electron backscatter diffraction) between adjacent disks, and thus complementary dihedral angles can be measured as a function of variable lattice coincidence.

Ten synthetic quartz grain boundaries were exposed to pure H₂O over a range of induced crystal misorientations ranging from ~1° to 120° by rotations about the c-axis. It was expected that low-energy grain boundary configurations (e.g. 0° misorientation) would yield high dihedral angles. It was impossible to separate grain boundaries with misorientations <5° because the adjacent disks of quartz grew together to form a single crystal. Surfaces of quartz disks that were misorientated by values >5° yielded a narrow, normal distribution of dihedral angles ranging from 46° to 68° with a median value of 56°±4 (n=246). In natural quartzose rocks it is expected that there exists a large range of misorientations across grain boundaries. However, these results indicate that misorientation values >5° do not contribute to variable grain boundary energy or the spread of observed dihedral angles.

Oxygen diffusion "fast-paths" in titanite single crystals

X.Y. ZHANG, E.B. WATSON AND D.J. CHERNIAK

Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy, NY 12180 (zhangxy@rpi.edu, chernd@rpi.edu, wastoe@rpi.edu)

Natural titanites are far from perfect ideal crystals. In addition to point defects, which affect oxygen lattice diffusion, there might be line- or planar defects along which fast diffusion could occur. While experimentally measuring oxygen lattice diffusion in titanites, we found that almost all of the oxygen diffusion profiles for natural titanites departed from the complementary error function solution expected for simple lattice diffusion, instead having a "tail" reaching deeper into the samples. For both dry and hydrothermal experiments, ^{18}O was used as the diffusant. In dry experiments, the source material was ^{18}O -enriched SiO_2 powder, while ^{18}O -enriched water was used for the hydrothermal experiments. Diffusive uptake profiles of ^{18}O were measured in all cases by nuclear reaction analysis (NRA) using the $^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$ reaction.

The diffusion "tails" can be explained by either parallel planar defect or one-dimensional "pipe" models. In our experiments, different sizes of "tails" (with varying ^{18}O concentrations) were observed. Under the same temperature and pressure conditions, the sizes of tails were affected by two factors: the diffusion duration and the defect density. For the same experiment duration, the higher the defect density, the larger the "tail"; for the same defect densities, the longer the diffusion duration, the larger the "tail".

The oxygen diffusion rates in the fast-paths were obtained by traditional graphical analysis methods, using the Whipple-Le Claire equation (for 2-D defects) assuming that the width of the fast path is 1nm. Two Arrhenius relations were obtained for the fast-path diffusion, one for experiments under dry conditions, the other for hydrothermal conditions:

$$D_{\text{dry}} = 4.03 \times 10^{-2} (\text{m}^2/\text{sec}) \exp(-313 \pm 22) (\text{kJ}/\text{mol}) / RT$$

$$D_{\text{wet}} = 3.48 \times 10^{-7} (\text{m}^2/\text{sec}) \exp(-219 \pm 39) (\text{kJ}/\text{mol}) / RT$$

AFM imaging of HF etched titanite surfaces suggest that the diffusion fast-paths might be either parallel planar defects or parallel pipe defects.

In addition to the lattice diffusivity, the presence and 3-D distribution of any fast paths—and the diffusivity in these paths—is important to the bulk closure properties of single crystals. For titanites, AFM imaging showed that the fast-paths may not be interconnected at a length-scale comparable with the crystal dimension, so they may not have a dramatic effect on bulk closure properties.

Effects on a basaltic surface of an impact-derived hot fluid bed (Kirbet-el-Umbachi, Syria)

M.-A. COURTY¹, M. FEDOROFF², M. MERMOUX³ AND D. SMITH⁴

¹UMR 5198, CNRS-IPH, CERP. Av. Léon-Jean Grégory, 66720 Tautavel, France (courty@tautavel.univ-perp.fr)

²ENSCP. 11 rue Pierre et Marie Curie, 75231 Paris, France (michel-feodoroff@enscp.jussieu.fr)

³LEPMI-ENSEEG, Dom. Univ., BP75, 38042 Saint-Martin d'Hères, France (michel.mermoux@lepmi.inpg.fr)

⁴MHN, Laboratoire de Minéralogie, 61 rue Buffon, 75005 Paris, France (davsmith@mnhn.fr)

Evidence for widespread dispersion of impact ejecta micro-debris at ca. 4-kyr-BP was recently investigated from archives in lands and seas. Regional diversity of surface effects linked to the ejecta fallout that range from moderate heating to localized melting raised questions about the nature and composition of the impact cloud when reaching the soil surface. The most extensive melting caused by the ejecta fallout has been reported as a unique bone-rich basaltic breccia over ten square metres at Kirbet-el-Umbachi (Syrian desert). The aims of the present study are to elucidate composition of the ejecta, its interaction with the host materials, and its significance in terms of impact-related processes. This is achieved by *in situ* analytical characterization based on high resolution SEM, WDS microprobe, and Raman spectrometry. The basaltic breccia displays a complex imbrication of anomalous petrographic facies that are distinctive from the local basalts. The unique suite of carbonaceous polymorphs (nano-sized diamonds, graphitic carbon, PAH species and amorphous carbon) in the recrystallised materials trace the carbonaceous component of the 4-kyr BP impact ejecta. Heterogeneous tear-dropped clasts that are embedded in the recrystallised basalts consist of Ca-rich silicate glass with heterogeneities indicating silicate-carbonate immiscibility, diaplectic quartz, barium sulphate, and diverse re-crystallized phases (silico-phosphate, Ca-phosphates, silicates). They trace solidified debris from the ejecta melt that derived from partial melting of carbonates, silicates, phosphates and soluble salts. Occurrence of a cm-thick crust with abundant domains of heated to melted bone fragments and a flow acicular facies is explained to result from high temperature (1200-1400°C) interaction between CO_2 -rich hot intrusive fluids and materials present at the surface: animals, basalts, and calcareous soils. Heating and selective melting over a few square meters would trace the exceptional pulverisation of a large mass of hot liquid melt with solid debris, in contrast to the widespread spray of hot fine debris in other regions.

Dissolution of oil well cement in presence of CO₂/H₂S under HTHP

J. CENTENO¹, A. RAMIREZ¹, A. COLINA²
AND A. BLANCO²

¹Instituto de Ciencias de la Tierra, UCV, Venezuela.
(centenojs@pdvsa.com)

²PDVSA –INTEVEP, Los Teques, Venezuela
(colinaa@pdvsa.com; blancoa@pdvsa.com)

Introduction

The cement material used in the construction of deep oil well reservoirs is frequently exposed to high temperatures and pressures (HTHP) and to the corrosive action of gases like CO₂ and H₂S, presents in the media, that can alter its properties. According to the criterion of Nickel (1995), the cementing material can be considered as a mineral mixture. In this study the interactions between the cement material and CO₂/H₂S are investigated to establish a method for optimal selection of cylindrical cement samples of two different dimensions (1" x 2" and 1/2" x 1").

Methods

Samples were exposed to the action of a mixture of CO₂/H₂S, dissolved in water, in a Parr reactor for HTHP (T= 160 °C; P_{CO2}= 37.77 atm; P_{H2S}= 16.33 atm; P_T= 102.07 atm) to compare their dissolution rates on laboratory scale and chose the most suitable geometry. The reaction times were 1, 3 and 7 days. The test solution was analyzed by Inductive Coupled Plasma -ICP- (elements) and Ionic Chromatography (anions). Dissolution rates were calculated and the Na/Ca and K/Ca relations were compared.

Results and Conclusions

After performing laboratory tests, it was observed severe damage (leached) in the samples exposed to the mixture of CO₂/H₂S within different time scales. The results obtained for Na, K, Ca, suggested that 1/2" x 1" samples show important benefits in terms of time laboratory constraints compared with the 1" x 2" dimensions. This statement is strongly supported by a chemical study. These results will be used in further studies of mechanical properties and mineralogical composition of cement material in aggressive conditions.

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Geochemical feature of chlorites in No. 201 and No. 361 uranium deposit, South China

RENMIN HUA, ZHANSHI ZHANG AND JUNFENG JI

State Key Laboratory for Mineral Deposit Research,
Department of Earth Sciences, Nanjing University,
Nanjing 210093, China. (huarenmin@nju.edu.cn)

The No.201 and No.361 uranium deposits are genetically related with the Zhuguang granite pluton. Chloritization was one of major hydrothermal alterations and some chlorites were very closely associated with uranium mineralization. Chemical compositions of the chlorites analyzed from EPMA are: SiO₂ = 28.81~22.20%, Al₂O₃ = 22.38~15.79%, FeO = 39.74~26.18%, and MgO = 15.45~3.47%, attributed mostly as prochlorites or ferromagnesian chlorite. They are Fe-rich species and formed under a relatively reductive environment. However, the wider range of FeO and MgO concentrations indicated that some of the chlorites might formed from an Fe- and Mg-enriched fluid.

In the n(Mg)/n(Fe+Mg) vs. n(Al)/n(Al+Mg+Fe) diagram (Laird, 1988), most chlorites have a source of argillaceous rocks, which was the source of the granites in that area. But less chlorites seem to have sources similar to mafic rocks or related fluids. The forming temperatures of chlorites were calculated from the T-d001 equation of Battaglia (1999). Chlorites in granite formed at 276~220°C, while those related to later diabase dyke 241~169°C.

It is postulated that there are two forming mechanisms of chlorites in the studied area. One was resolving-precipitating, and the other was resolving-migrating-precipitating. The later was represented by the chlorite veinlets occurred in the fissures. The close spatial relation between these chlorite veinlets and uranium ore revealed that the chloritization in these two deposits not only reactivated and transported uranium from granite, but can also adsorb and precipitate the uranium to form ore-bodies.

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