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GENESIS OF THE POLLYMETALLIC ORE DEPOSIT GHEZURI, ROMANIA - CONCEPTUAL MODEL

Monica Radulescu (mirunache@comtrust.ro)¹,
Grigore Buia (buia@upet.ro)¹ &
Gheorghe Popescu (ghpop@geo.edu.ro)²

¹ Universitatea din Petrosani, Str. Universitatii 20, Petrosani,
2675, Romania

² Universitatea Bucuresti, Facultatea de Geologie, Bd. N.
Balcesu, Romania

The geologic features of the mineralized structure Ghezuri suggest a hypoabasic intrusion represented by microdiorites with pipes intruded in the microgranodioritic porphyritic volcano. Related to it, a lead-zinc mineralization vein system has been formed. The geologic and metallogenetic context allowed the development of the following metallogenetic scenario (Buia, 1998): During the end of pontian a subvolcanic body has been intruded along a faulty structure concordant to the NNW-SSE direction. Lately, it has been penetrated by a microdioritic intrusion related to postmagmatic fluid mineralizations containing mineralizers (OH⁻, H₂O, CO₂, HCl) migrating upwards along the two faults. In the meantime, the three water types (metamorphic, connate and meteoric) have been circulated. The hydrothermal solutions generating the polymetallic deposits from Ghezuri have an important content in connate water. The intense vaporization of the fractures and aquifers water increased the external pressure, suppressing the internal one. Due to these conditions, the water from the surrounding strata is absorbed by the ascending magma. The water takes from the magma and the surrounding rock components that are deposited lately. The mixture occurred probably on the upper parts, at the level of the sedimentary intrusion, between the intrusive microgranodioritic body and the hyaloandesitic pyroxenic lava flows, fact argued by the massive galena deposition below this level. During the primary state, the internal pressure of the lava and the separate solution is greater than the external pressure, so the infiltrating water can not penetrate the magma. The main deposition mechanism of the elements from solutions is represented by filling the vacuoles, the metasomatism being active only in the contact zones. The reaction of the mineralizing solution with the host rocks produced the saturation and the deposition of the metallic components. The Ghezuri mineralization, by its characteristics can be grouped in the epithermal type mineralization, the law-sulphidation facies, with basic metals and silver sulphides, formed at high temperatures (Popescu, 1885).

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ULTRASONIC EXPERIMENTS IN AN INTERNALLY HEATED GAS-PRESSURE VESSEL UNDER ELEVATED P-T CONDITIONS

Juliane Ramelow (jule@gfz-potsdam.de),
David Bruhn & Frank R. Schilling

GFZ-Potsdam, Division 4, Telegrafenberg, 14473 Potsdam,
Germany

Dehydration reactions and partial melting are important to understand geodynamic processes and the evolution of the Earth's crust. Ultrasonic experiments are used to study these processes in the laboratory under in-situ conditions. Both, dehydration reactions and partial melting often occur at temperatures and pressures exceeding the limits and conventional ultrasonic experiments. We will present an experimental setup to determine sound wave velocities of rocks at elevated pressures and temperatures, especially designed to measure sound wave absorbing materials, such as partially molten rocks. The sample size for ultrasonic experiments is predefined by the grain size of the sample and the wavelength of ultrasonic waves. The wavelength should be at least 3-5x of the maximum grain size and the diameter of the sample should be at least 2.5 times of the wavelength. The absorption of ultrasonic waves strongly increases with increasing frequency. As a consequence, low frequencies are required to study sound-wave velocities of strongly absorbing materials. However, at low frequencies bigger samples are a prerequisite to measure P-wave velocities. An internally heated gas-pressure vessel (Harwood) for pressures up to 1 GPa is modified to measure simultaneously P- and S-wave velocities on cylindrical samples with a diameter of 29.5 mm and a length of 25 mm. To avoid uncontrolled degassing, the sample is encapsulated in a Ni- or Ni-alloy tube. Transducers are glued on ceramic buffer rods at their cold-ends. Sound velocities were deduced from travel-times measured both in pulse echo and pulse transmission mode. The measuring scheme allows correcting for the temperature and pressure depending travel-time through the buffer rods. We will present experimental results up to 1 GPa and temperatures exceeding 900°C. Some data on amphibolites and serpentinites will be discussed.

PHASE TRANSITION IN THE MINERAL TITANITE CaTiOSiO₄ UNDER HIGH PRESSURE - A X-RAY SINGLE CRYSTAL STUDY BETWEEN 1 BAR AND 10 GPa

Stephanie Rath (rath@kristallerdw.ethz.ch)¹,
Martin Kunz² & Ronald Miletich¹

¹ Department of Earth Sciences, ETH Zurich, 8092 Zurich,
Switzerland

² Department of Earth Sciences, University of Basel, 4056
Basel, Switzerland

The monoclinic mineral titanite is a common accessory in many acid and intermediate igneous rock, gneisses, mica schists and amphiboles. The structure of titanite is characterized by corner-linked chains of TiO₆ -octahedra parallel to [100] connected via isolated SiO₄ -tetrahedra. CaO₇ polyhedra build chains along [101]. The octahedral Ti atoms show typical out-of-center distortions. Its behavior under high pressure can give information about the driving forces of the phase transition in ABOCO₄ silicates. The behavior of titanite under high pressure has been studied up to 7 GPa and 850 K with powder diffraction, respectively (Angel et al., 1999; Bismayer et al., 1999;

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Kunz et al., 2000) and several phase transitions were found. The structure remains monoclinic but changes from $P2_1/a$ to $A2/a$ at 3.6 GPa.

Here we present evidence for a new $A2/a - A\bar{1}$ phase transition at around 10.5 GPa. At this pressure the cell metric decreased to the following values: $a = 6.829(4)\text{\AA}$, $b = 8.594(2)\text{\AA}$, $c = 6.352(1)\text{\AA}$, $\alpha = 90.18(2)^\circ$, $\beta = 112.78(2)^\circ$, $\gamma = 89.70(2)^\circ$ and $V = 343.7(2)\text{\AA}^3$.

Structure refinement results of high-pressure X-ray single crystal studies from ambient conditions to 10 GPa will be presented. In addition, we compare the titanite results to the phase transition in the topological identical malayaite CaSnSiO_4 at 5 GPa, where a similar phase transition has previously been observed (Rath et al., 2002).

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ELASTICITY OF SODIUM-RICH MAJORITE

Hans Josef Reichmann (hanni@gfz-potsdam.de)¹, Stanislav V. Sinogeikin (stas@hercules.geology.uiuc.edu)², Jay D. Bass (bass@hercules.geology.uiuc.edu)² & Tibor Gasparik (gasparik@sbmp04.ess.sunysb.edu)³

¹ Geoforschungszentrum Potsdam PB 4.1, Telegrafenberg, 14473 Potsdam, Germany

² Department of Geology, University of Illinois, Urbana IL 61801, U.S.A.

³ Department of Geosciences, State University of New York at Stony Brook, Stony Brook, NY 11794-2100, U.S.A.

Majoritic (aluminum-deficient) garnet is a major component of the upper mantle and the Transition Zone. Therefore the knowledge of the elasticity of majoritic garnets is extremely important for understanding the composition and behaviour of this region, as well as subduction-related processes. The variation of elastic properties within the pure Mg pyrope - majorite solid solution is well constrained. However, the effect of large cations on the elasticity of majorite-garnet solid solutions is poorly determined, even though large cations such as Na and Ca are important constituents of any realistic petrologic model of the Earth's mantle. In particular, oceanic crust subducted to transition zone depths will transform to an assemblage in which Na-rich majorite is an abundant phase.

Here we present the first Brillouin measurements on the elasticity of majorite with a composition on the enstatite-jadeite join. A polycrystalline sample with a composition of 50 mol% enstatite - 50 mol% jadeite (En50-Jd50) was synthesised in a large volume press at 22 GPa and 2000°C at the Center for High Pressure Research, Stony Brook. An x-ray spectrum of the sample indicated the presence of a majorite phase only, and no peaks of a second phase were observed.

The bulk modulus ($K_s = 171.6(35)$ GPa) of En50-Jd50 majorite is characteristic of other majorites and aluminous garnets, indicating that the bulk modulus is remarkably insensitive to

composition. However, the shear modulus increases significantly with increasing Na content, reaching a value of 103.5(20) GPa for En50-Jd50 majorite. This shear modulus is over 20% higher than the shear modulus of En100 majorite. An analysis of available elasticity data on pyroxenes and majorites indicate that the shear velocity jump associated with the pyroxene-majorite transition will dramatically increase with increasing jadeite content of the system.

NETWORK MODIFIER AND TRACE ELEMENT DIFFUSION IN DIOPSIDE LIQUID AT HIGH PRESSURE

Joy E. Reid (joy.reid@uni-bayreuth.de), Brent T. Poe & David C. Rubie

Bayerisches Geoinstitut, Universität Bayreuth, 95440 Bayreuth, Germany

Many models of core formation in the early Earth have assumed the presence of a global magma ocean, which would have allowed chemical equilibration between metal and silicate to depths of up to 1000 km. The kinetics of equilibration would depend to a large extent on the transport properties of the silicate and metal liquid systems, for example, ionic diffusion and viscosity. It has been previously proposed that the diffusion of network modifying ions and trace elements in silicate liquids will be inhibited by pressure. Ca and Mg self-diffusion and Co and Ni trace element diffusion in diopside ($\text{CaMgSi}_2\text{O}_6$) liquid have been determined at high pressure. Diffusion couples enriched in ^{44}Ca and ^{25}Mg and doped with trace quantities of CoO and NiO were pressurised and heated in a multianvil apparatus. Experimental charges were subsequently analysed by ion microprobe at the University of Edinburgh and the resulting profiles fitted using a non-linear least-squares approximation for self-diffusion between two finite bodies. Quantitative results for all elements from 4 to 8 GPa confirm a negative activation volume of $-2\text{ cm}^3/\text{mol}$ and preliminary results indicate a continued increase in diffusivity to 15 GPa. This behaviour is in contrast to that of network forming ions Si and O, which show a positive activation volume to 10 GPa after which there is a change of slope and an increase in diffusivity to 17 GPa. It can be concluded that there is little diffusive coupling in diopside liquid, in this pressure range, between the network formers and modifiers or between the network formers and trace elements Co and Ni.

RHEOLOGICAL CONSTRAINTS ON MELT MIGRATION

Joerg Renner (renner@geophysik.ruhr-uni-bochum.de)

NA 3/156, GMG/RUB, D-44780 Bochum, Germany

The chemical differentiation of the Earth is related to flow of melts through rocks transporting heat and material and altering composition. Interpreting geochemical analyses of rocks depends on how the composition of the melt is affected by the migration processes. Substantial experimental effort was invested into constraining theoretical models of the relationships between deformation and melt extraction by laboratory studies on permeability and matrix rheology of partially molten aggregates. From an experimental point of view, migration of basic melts in the upper mantle largely responsible for the formation of oceanic crust at mid-ocean ridges is distinct from

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transport of felsic magmas involved in the development of continental crust. The pore space of partially molten peridotites is regular and interconnected. Constraints on the relationship between permeability and porosity/melt fraction can be derived from theoretical models that assume equal-sized, texturally-equilibrated grains. In contrast, the partial melt resides in irregular, often angular and isolated pockets in granites. For fluid-filled aggregates, strength depends on effective pressure, the difference between matrix and pore fluid pressure. Permeability determines whether a constant pore pressure can be maintained during deformation. Compaction rates measured for partially molten peridotites at controlled melt pressure provide estimates of the permeability and bulk viscosity of the Earth's upper mantle that can be used to calculate compaction length, the characteristic length scale of continuum mechanical models. Triaxial deformation experiments on partially molten peridotites revealed that shear viscosity experiences a modest reduction for melt fractions <0.05 . The reduction is significantly greater at larger fractions related to excessive, loading-related wetting of two-grain boundaries. At the comparatively lower solidus temperatures of granites, feldspar deforms by a combination of brittle processes and low-temperature plasticity. Consequently, dilation rate becomes important leading to a rate dependent critical melt fraction.

HIGH PRESSURE PHASE RELATIONS AND PHYSICAL PROPERTIES OF MATERIALS IN THE EARTH'S MANTLE

Bruno Reynard (breynard@ens-lyon.fr)

Department of Earth Sciences Earth Sciences, ENS Lyon, 46 Allée d'Italie, F-69007 Lyon, France

Phase relations are essential for understanding of the structure of planetary interiors and the differentiation of planetary bodies. The knowledge of the stable phases and of their elastic properties allows to decipher the seismic profile of density, compressional and shear wave velocities in terms of the constitutive mineralogical and liquid phase assemblages and to constrain the bulk chemistry and thermal state, provided the physical properties of interest are measurable under the relevant conditions. Over the past three decades, there have been a lot of improvements in that research field that now allow to measure or simulate the structure and properties of geomaterials at high pressures and temperatures. We focus here on developments in experimental techniques for in situ measurements applied to systems allowing to predict the mineralogical composition of the Earth's mantle.

Examples are given to show that integrated studies of a given material (major ferro-magnesian silicates, carbonates) with room-temperature X-ray diffraction for equation of state determination (RTEoS), HP-HT EoS determinations, HP-HT Raman spectroscopy and vibrational modeling of the thermal contribution to EoS and free enthalpy, allow to completely describe its thermodynamics and to model its phase relations. The required degree of precision for accurate modeling in the mantle pressure range is discussed in order to emphasize the new developments required in physical property measurements at HP-HT.

ROLE OF Si/Al RATIOS ON THE CELL PARAMETERS OF SYNTHETIC LEUCITE ANALOGUES

Elizabeth Rodrigues (beth@ufpa.br) & Jacques Roux

The aim of this work was to evaluate the role of Si/Al ratios on the cell parameters of synthetic leucite analogues: analcime ($\text{NaAlSi}_2\text{O}_6\text{H}_2\text{O}$), pollucite ($\text{CsAlSi}_2\text{O}_6$) and Rb-leucite ($\text{RbAlSi}_2\text{O}_6$). This study was based on systematic investigations of the variation of Si/Al ratios on stability domains of leucite analogues and the deviation from stoichiometric Si/Al ratio in the analcime – pollucite and analcime – Rb-leucite solid solutions. On analcime, cell parameters are indirectly related to the Si/Al ratios. Analcimes with $\text{Si/Al} < 2.0$ presented nepheline like addition phase, even though at analcimes with $\text{Si/Al} > 2.0$, albite was detected. In leucite analogues, cell parameters are independent of Si/Al ratios. At 600°C - 5.5, 2.0, 1.0 kbar, all pollucites studied yield a similar value of cell parameter. Cs-nepheline was observed like subordinated phase on $1.15 < \text{Si/Al} < 1.7$ pollucites and quartz on $2.69 < \text{Si/Al} < 3.0$ pollucites. On Rb-leucite, at 3.5 kbar - 600°C and 900°C , all $1.15 < \text{Si/Al} < 2.67$. Rb-leucites presented identical cell parameters. An Rb-feldspar phase co-exist with the Rb-leucite for $\text{Si/Al} \sim 2.12$ until ~ 2.67 . The Rb-feldspar presented the same cell parameters than the natural Rb-feldspar, rubicline (Teerstra et al., 1998). Analcime – pollucite Si/Al ratios yielded a significant deviation from 2.0 stoichiometric value, and could reach 2.41 with increasing amounts of Cs in the join. However, analcime – Rb-leucite Si/Al ratios are not affected by the variation of amounts Rb. At both solid solutions, the cell parameters decrease with the increase of heavy cations amounts. In analcimes S sites are filled up by Na, while they are void in leucite analogues. T sites Al occupation is linked to the occupation of S sites, then only analcimes presented a direct relationship between Si/Al ratios and cell parameters.

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CRYSTALLISATION PROCESSES OF CALCIUM ALUMINOSILICATES NEAR THEIR GLASS TRANSITION

Mathieu Roskosz (roskosz@crpg.cnrs-nancy.fr)¹, Mike Toplis (mtoplis@crpg.cnrs-nancy.fr)¹, Pascale Besson (besson@ipgp.jussieu.fr)² & Pascal Richet (richet@ipgp.jussieu.fr)²

¹ Centre de recherches pétrographiques et Géochimiques, 15 rue notre-dame des pauvres BP 20, 54501 Vandoeuvre-lès-Nancy cedex, France

² Laboratoire de Physique des Géomatériaux, IPGP, 4 place Jussieu, 75252 Paris cedex 05, France

Although crystallisation in silicate melts has been the subject of numerous studies, the chemical and structural factors affecting nucleation and crystallisation are still poorly understood, in particular at temperatures below the solidus. In order to assess the fundamental controls affecting the kinetics of crystal nucleation/growth and phase composition below the solidus, we have undertaken a systematic study of crystallisation in calcium aluminosilicate liquids just above their glass transition. A wide range of composition has been studied with silica

content from 33 to 70 mol%, principally along two joins with molar $\text{CaO}/(\text{CaO}+\text{Al}_2\text{O}_3)$ of 0.78 and 0.52. Typically, samples have been heated for 3 to 24 hours, between 30 and 100K above their glass transition. We have determined textures, compositions and unit-cell parameters of the crystalline phases over a wide range of length scales, using optical and electron microscopy (SEM, TEM), Electron microprobe, X-ray diffraction (XRD) and raman spectroscopy.

The results show that in the majority of cases the first phase to crystallise is not the liquidus phase but may be one of the solidus phases. With the exception of compositions close to 'anorthite', the Si/Al ratio of the first phase to precipitate is as close as possible to that of the parent liquid, consistent with the rapid diffusion of Ca compared to that of Si and Al (Gruener et al., 2001). Different mechanisms of crystallisation have been observed, including isochemical crystallisation of metastable phases, and fine scale intergrowth of (often highly substituted) stable phases. A schematic map of the compositional domains in which different low-temperature crystallisation processes occur will be presented. Furthermore, the kinetics of crystallisation are found to be decoupled from viscosity, despite the fact that diffusion and viscosity are commonly key parameters in theories of crystal growth and further work to understand these results is in progress.

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KINETIC CONTROL ON LIQUID COMPOSITION AND PHASE RELATIONS FROM COOLING EXPERIMENTS ON STROMBOLI LAVAS (AEOLIAN ISL., ITALY)

Silvio Giuseppe Rotolo (silrot@unipa.it)¹, Aida Maria Conte², Ida Di Carlo¹, Cristina Perinelli³ & Raffaello Trigila³

¹ Dip. Chimica e Fisica della Terra, Università di Palermo, Via Archirafi 36 90123 PALERMO, ITALY

² Ist.di Geoscienze e Georisorse - C.N.R. c/o Dip. Scienze della Terra, Univ. La Sapienza., P.le A.Moro 5, 00185 Roma, ITALY

¹ Dip. Chimica e Fisica della Terra, Università di Palermo, Via Archirafi 36 90123 PALERMO, ITALY

³ Dip. di Scienze della Terra, Università La Sapienza, P.le A.Moro 5, 00185 Roma, ITALY

³ Dip. di Scienze della Terra, Università La Sapienza, P.le A.Moro 5, 00185 Roma, ITALY

Cooling experiments performed at $P=1$ atm., T in the liquidus-solidus region and $f\text{O}_2 = \text{NNO}$, on 4 Stromboli lava samples ($\text{SiO}_2 = 50.0\text{-}54.4$ wt%) of CA, HK-CA, SHO, KS affinity put in evidence the kinetic control, due to the different melt viscosities, on phase relations and on the evolution of the experimental liquids. Starting compositions, in form of finely ground powders, have been firstly raised to superliquidus temperatures ($>1230^\circ\text{C}$) for three hours, then cooled at $900^\circ\text{C}/\text{h}$ or $1^\circ\text{C}/\text{h}$ respectively to the experimental temperature keeping a final isotherm of at least 36h and finally quenched.

The effect of the two different cooling gradients was to produce a unique liquid line of descent for each starting composition with modest compositional gaps between fast and slow cooling rates, gradually increasing at lower temperatures. Additional records of metastable equilibria due to the differential liquid

cooling rate come from phase relations and phase compositions. In the slow cooling rate runs the usual crystallisation sequence is given by plag- cpx- ol-(pig). Pigeonite is absent in the natural starting compositions but it crystallizes in the CA sample across both cooling gradients. In the HK-CA sample pigeonite crystallizes before olivine and Ca-clinopyroxene in the slow cooling rate runs, being absent in the fast gradient ones. As expected, both SHO and KS samples do not show this phase. In CA and HK-CA composition, clinopyroxene shows a remarkable temperature dependence but it does not vary significantly in the two series of experiments. On the contrary, clinopyroxene from SHO and KS samples shows a narrow compositional range.

Other experiments are in progress to compare these data with those obtainable through thermodynamic calculations that express the real conditions of thermodynamic equilibria. In any case it is evident that the kinetic control affects, in some compositions, the pigeonite stability. By calibrating opportunely this effect it is possible to gain some indication on the magma ascent speed and therefore on the volcanic hazard.

EXPERIMENTAL DETERMINATION OF ZIRCON-GARNET-MELT TRACE ELEMENT PARTITIONING AND ITS APPLICATION TO DATING

Daniela Rubatto (daniela.rubatto@anu.edu.au) & Jörg Hermann (joerg.hermann@anu.edu.au)

Research School of Earth Sciences, Australian National University, Canberra 0200 ACT, Australia

Garnet is the mineral most used for thermobarometry, whereas zircon is a widely used chronometer: the relative timing of their growth is thus an important information for P-T-time reconstruction. We aim to determine the coexistence of zircon and garnet by trace element partitioning.

We carried out piston cylinder experiments at conditions of $P = 20$ kbar and $T = 750\text{-}1050^\circ\text{C}$ in the system $\text{Na}_2\text{O-K}_2\text{O-CaO-FeO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$. The starting material has been doped with Zr and trace elements (P, Ba, Y, Hf, REE, Th and U) and contains 8-10% H_2O . The run products include 50-90% of hydrous granitic melt, 5-20% of garnet, ca. 3% of zircon and additional phases such as allanite, staurolite, micas, pyroxenes, quartz and monazite. We were able to produce large (up to several $100\mu\text{m}$ in diameter) and homogeneous garnet, but zircon grain size was always smaller than $5\mu\text{m}$. A combination of electron microprobe, laser ablation-ICPMS and ion microprobe (SHRIMP-RG) analysis have been used to obtain the trace elements composition of the phases.

Y and HREE strongly partition into garnet with respect to melt ($D = 20\text{-}80$); the distribution coefficients for MREE, Zr and Hf are close to unity; whereas Ba, LREE, Th and U preferentially enter the melt. With respect to garnet, zircon incorporates higher amounts of most MREE, HREE and in particular Zr, Hf, U and Th. Results are consistent with mass balance calculation and data from natural samples.

Zircon-garnet partitioning has been applied to natural samples to determine the coexistence of zircon and garnet zones. This allows correlating the age of selected zircon domains to metamorphic conditions obtained from garnet.

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A RAMAN SPECTROSCOPIC STUDY OF THE INTERMOLECULAR INTERACTIONS IN WATER AND THEIR DEPENDENCE ON ELECTROLYTE CONCENTRATION

Fernando Rull (rull@fmc.uva.es)¹ & Jean Dubessy (jean.dubessy@g2r.uhp-nancy.fr)²

¹ Cristalografía y Mineralogía, Facultad de Ciencias, 47005-Valladolid, Spain

² UMR G2R Faculté des Sciences, 54506-Vandoeuvre lès Nancy Cedex, France

The knowledge of structural properties of aqueous solutions is of capital importance in the understanding of the transport properties, crystal growth and mineral formation in the earth crust. These properties are, in their turn closely related to the molecular and ionic interactions between solvent molecules and solvent-solute molecules. It is well known that vibrational spectroscopy and particularly Raman spectroscopy is a powerful tool in the quantitative analysis of these interactions. In the context of a long study of the dynamical properties of water and inorganic aqueous solutions undertaken in our laboratory at Valladolid and Nancy (Rull and Saja 1986, Rull et al. 1995, Rull and Ohtaki 1997, Dubessy 1999) we present here recent results related with the influence of the salt concentration on the dynamics of water molecules and polyatomic anions when dissolved in H₂O, D₂O and H₂O/ D₂O mixtures at room temperature. The systems studied were salts of type X_nY_m (where X=Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Mg²⁺, Zn²⁺ and Y= Cl⁻, ClO₄⁻, NO₃⁻, SO₄²⁻). Raman spectra were taken in the conventional 90° configuration using polarised light and in retro mode using a micro-Raman and depolarised light. In the present work interest has been focussed in the study of internal vibrations of water and hydration bands of cations. The ν(OH) band undergoes strong modifications in intensity and band profile on the concentration of different salts. These modifications, depends mainly on the nature of anions while cations have a weak influence. The quantitative analysis of these changes is subjected to several difficulties due to the intrinsic overlapping of the components bands to the whole envelope. To introduce new insight in this analysis a combined methodology joining the capabilities of the self-resolution and new band-fitting methods is used. Of particular importance is the study of aqueous solutions using as solvent H₂O/ D₂O mixtures in which the vibrational decoupling induced by isotopic substitution simplify the band profile analysis. From these results a precise model of vibrational water bands is suggested and discussed.

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EXPERIMENTAL AND THERMODYNAMIC MODELING OF POTASSIUM-BEARING CLINOPYROXENE EQUILIBRIA IN THE SYSTEM CaMgSi₂O₆-KAlSi₂O₆

Oleg G. Safonov (oleg@iem.ac.ru)¹, Luca Bindi (lbindi@steno.geo.unifi.it)², Yuriy A. Litvin (litvin@iem.ac.ru)¹, Leonid L. Perchuk (lper@geol.msu.ru)¹ & Silvio Menchetti (lbindi@steno.geo.unifi.it)²

¹ Institute of Experimental Mineralogy, Moscow district, Chernogolovka, 142432, Russia

² Dipartimento di Scienze della Terra, University of Florence, Via La Pira 4, Florence, Italy

Potassium-bearing clinopyroxene (KCpx) is characteristic for high-pressure magmatic and metamorphic environments, and it is considered as a potential reservoir for potassium in the deep mantle (e.g., Harlow & Veblen, 1991; Sobolev & Shatsky, 1990). The KCpx is the diopside (Di)- "K-jadeite" (CaMgSi₂O₆-KAlSi₂O₆) solid solution whose thermodynamic properties are unknown so far. We experimentally studied the join CaMgSi₂O₆-KAlSi₂O₆ (e.g., Luth, 1992) at 7 GPa and 980-1650°C using the "anvil-with-hole" assembly (Litvin, 1990). The KCpx solid solution is the liquidus phase (Perchuk & Yapaskurt, 1998) in the diopside-rich portion of this pseudo-binary system, while grossular-rich garnet presents at the liquidus on the K-rich portion of the diagram. The K₂O content in the KCpx increases from the melting point of pure diopside up to 5.5 wt.% K₂O at ~1300°C. The crystal structure of KCpx with 5.0 and 1.57 wt.% of K₂O was refined by the x-ray method. This substitution K for Ca causes strong modifications of the average structure, reflecting mainly in the enlargement of the M2 polyhedron. No evidence for Mg in the M2 site as a structural stabilizer for K in the K-Cpx structure (i.e. Harlow, 1996) was found. The thermodynamic treatment of existing experimental data on KCpx-melt equilibria within 1100-1900°C and 1.5-11 GPa for wide range of silicate systems allowed to describe the KAlSi₂O₆ content in KCpx on the basis of the equilibrium $KAlSi_2O_6 = 1/4K_4Si_2O_6 + 3/4Al_{4/3}Si_2O_6$ (in melt) with the accuracy ±0.91 GPa and ±1.2 mol.% of KAlSi₂O₆ in KCpx. The study is supported by the Russian Foundation for Basic Research (projects 01-05-64775 to OGS), the Program "Leading Scientific Schools" (project 00-15-98519 to LLP) and the Integration Program of Russian Academy of Science (project A0113 to YAL).

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