

EMPG IX

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

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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

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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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EMPG IX

Ninth International Symposium on Experimental Mineralogy, Petrology and Geochemistry

MINERALOGY AND FORMATION CONDITIONS OF THE MANTLE XENOLITHS FROM THE ALKALINE BASALTS OF TARIAT AND DARIGANGA PLATEAUS, MONGOLIA

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The mantle xenoliths permit us to study the composition, the structure and thermal state of mantle. In the present work the spinel(Sp)- and garnet-spinel(Sp-Gar)-bearing peridotites and pyroxenites from the Cenozoic alkaline basalts from the Central (Tariat plateau) and South-East (Dariganga plateau) Mongolia are studied. The main minerals are the Cr-rich diopside, orthopyroxene (Opx)(>En₈₅₋₉₀) and olivine (Ol) (>Fo₉₀). The accessory minerals are Sp (MgAl₂O₄ - FeAl₂O₄ - MgCr₂O₄ - FeCr₂O₄) and pyrope. The secondary minerals (phlogopite, magnetite, alkaline pyroxenes, pyrotite) are found also. These minerals were formed by mantle metasomatism. The composition of main minerals slightly varies. The primary zoning is absent. The signs of light deformation of rocks are established. The valency state of iron in the Opx, Cpx, Ol, Sp and Gar is determined by Moessbauer spectroscopy. High disorder degree of Fe²⁺ in the structure is revealed. The rocks composition shows their different depleting degree. By the ratio Ca/Si the rocks are divided into low (>0.09), middle (0.09-0.06) and high depleted (<0.06). The T and P for Sp-Gar rocks are determined by Gar-Opx geothermobarometer. T for Sp rocks is evaluated by Cpx-Opx and Ol-Cpx geothermometers. P is determined by geotherm for the Mongolia region. The Sp rocks were formed at 1000-1300°C and 25-40 kb, the Sp-Gar rocks at 1300-1550°C and 35-50 kb. The disorder degree of Fe²⁺ and Fe³⁺/Fe²⁺ are caused by high temperature crystallization and quenching during eruption.

IN SITU MEASUREMENT OF THE SOLUBILITY OF STRONTIANITE AT HP-HT CONDITIONS

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Subducted oceanic crust carries large quantities of volatile species, mostly as hydrous minerals (e.g. serpentines, amphibole, chlorite, micas, lawsonite,...) and as carbonates. In the course of subduction, these minerals break down and the

volatile species, H₂O and CO₂, are liberated into the mantle through dehydration/decarbonation reactions. The fluid phases thus produced, i.e. aqueous solutions enriched in various ionic species (trace elements such as Rb, Sr, Ba, Pb, U,...), react with the mantle, inducing melting, eventually leading to arc magmatism. It is therefore of great importance to constrain the chemical composition of these fluids and to study their reactivity toward silicates and carbonates. However, the composition of these deep fluids has remained highly uncertain, due to the lack of *in situ* studies.

X-ray fluorescence spectroscopy, thanks to its high sensitivity, is a powerful technique capable of determining quantitatively trace-element distribution and concentrations with micrometric resolution and ppm sensitivity.

We report here the first *in situ* experiments on the dissolution of carbonate minerals at pressures (up to 4 GPa) and at temperatures (up to 250°C) characteristic of subducted slabs. Using X-ray fluorescence, the dissolution of strontianite (SrCO₃), in rubidium-bearing aqueous solution, has been followed in a membrane-type diamond anvil-cell (MDAC) equipped with an external resistive furnace. Experiments were carried out at ESRF (ID22 micro-fluorescence beamline). Given the geometry of the MDAC, the fluorescence of Rb and Sr has been detected in transmission mode, at the rear side of the anvil. In order to use Sr/Rb ratio as a tracer of the dissolution process, fluorescence peaks of these elements (K α at 14.2 and 13.4 keV, respectively) have been calibrated first, using solutions of known Rb and Sr concentrations. These preliminary calibrations demonstrate that concentrations as low as 10⁻⁴M of Sr and Rb can be measured in a DAC.

Afterwards, we have measured the solubility of strontianite as a function of pressure at different temperatures. The results show that, at a given temperature, the dissolution rate increases as pressure increases, following the paradoxical behavior of carbonate minerals. This will allow further thermodynamic modelling of carbonate dissolution.

EXPERIMENTAL SEQUENCES OF SULPHIDES AND CARBONATE REACTIONS: AN ANALOGY OF THE MARINE SEDIMENTATION IN ANOXIC ENVIRONMENTS

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With the aim of establishing the relations that exist between certain types of minerals, sulphides and carbonates, in anoxic marine environments as well as to understand the factors and mechanisms that control the reactions that are necessary for their formation or dissolution, a number of laboratory experiments are carried out to simulate the sulphate reduction reactions in shallow water sediments of siliciclastic shelves in which the content and the reactivity of Fe is not a limiting factor. In the experiments a series of coupled reactions take place that cause the formation of amorphous iron sulphides and the formation of siderite. In addition the diagenetic environ-

ments for the formation of these components, sulphides and carbonates, in the sediments of the Bay of Cadiz are explained. The experiments which were carried out in an aqueous solution were designed taking into consideration that the bacterially-catalyzed sulfate reduction (Coleman, 1993) may be schematically expressed by means of the following reaction: $\text{CH}_3\text{COOH} + \text{SO}_4^{2-} \rightarrow \text{HS}^- + 2\text{HCO}_3^- + \text{H}^+$ (1). Thus aqueous solutions of 60 ml of distilled water were prepared to which 0.16 grms of sodium sulphide were successively added as a source for the formation of HS^- ions, and 0.10 grms of sodium bicarbonate as a source for the production of HCO_3^- ions. These concentrations allow for the ratio 1: 2 M between HS^- and HCO_3^- as can be observed in (1). Likewise 0.20 grms of aragonite were added which was extracted as a biogenic component of *Sepia Officinalis* and 0.5 grms of ferrous chloride as a source of Fe^{2+} ions. Under these conditions the pH of the solution was 6.88 and the experiments were carried out in inert N_2 atmosphere and the evolution of the experiments was monitored by checking pH. Immediately after adding the Fe^{2+} ions a decrease in the pH value as well as the presence of a black fine grain precipitation can be observed. Once the lower pH value has been reached a relative stabilization of the pH value (7.01) takes place. After a few days the precipitation is analysed by means of X-ray diffraction. The precipitation of siderite as well as the presence of an amorphous component can be concluded from the observation of the profiles. The last one is identified as FeS by EDS. These results can be interpreted on the basis of the decreasing variation of the pH whose values are balanced by the H^+ liberated in the formation of the FeS, which at first causes a quick decrease in the pH values until a certain value is reached. In a later stage and from this value onwards the decrease slows down due to the dissolution of the aragonite and the liberation of HCO_3^- until the value 6.88 and its relative stabilization at 7.01 is reached. During experiments carried out under absence of aragonite the pH reaches a value of 6.1. Thus the formation of siderite is possible once the necessary degree of supersaturation has been achieved which is the sum of the HCO_3^- content in the solution and that which is liberated through the dissolution of the aragonite. The formation of siderite is due to the presence of an excess of iron in the solution after the formation of FeS. Never was siderite detected when the molar proportion of Fe and S was the same, in that case calcite precipitates, or with lower proportions of Fe with respect to S.

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THE ELASTIC PROPERTIES OF MODEL BASALTIC MELT-COMPOSITIONS AT HIGH TEMPERATURES

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To constrain the effect of composition and temperature on the elasticity of glasses and super-cooled liquids, acoustic velocities of samples in the pseudo-ternary system anorthite-diopside-forsterite (An-Di-Fo) were measured by Brillouin

spectroscopy. Both the longitudinal and shear wave velocities where measured in the glassy state and into the region of super-cooled liquids. The glass transformation temperatures T_g inferred from the Brillouin measurements compared to previous studies are equal within the limits of experimental uncertainties. The variation of the elastic properties with temperature is approximately linear, both for the glassy state (below T_g) and in the super-cooled liquid state (above T_g). The temperature derivative of vibrational contributions to Young's (E), bulk (Ks), and shear (G) modulus is approx. 6-12x greater for super cooled liquids than for glasses. In the glassy state the elastic moduli and their temperature derivatives are described by ideal mixing of molar properties of oxides. The pronounced variations with composition in the elastic and anelastic properties above the glass transformation can be related to changes in configurational contributions. The configurational contribution for chemically complex glasses (mixtures of the An-Di-Fo end members) does not affect the overall compressibility at lower temperatures, whereas at higher temperatures they dominate the temperature derivatives of the moduli. The configurational contribution to compressibility is higher for complex compositions than expected from end-member compositions. Therefore, the density of complex melts in the basaltic anorthite-diopside-forsterite-system cannot be easily approximated from the behavior of pure anorthite or diopside samples. Our results indicate that with increasing temperature, configurations with a higher bonding strength were preferentially occupied. Isothermal relaxation times, varying between 0.01 and 1s at 950°C, show a minimum for intermediate anorthite-diopside-compositions and are related to the maximum in configurational entropy.

THERMODYNAMIC PROPERTIES OF Mg-Al-PHOSPHATES: POLYMORPHISM AND STABILITY OF MgAlPO_4O , A KEY PHASE IN THE $\text{MgO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ LAZULITE SYSTEM

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Ca-Mg-Al-phosphates (e.g. P-ellenbergerite, bearthite, lazulite, farringtonite...) have attracted increasing interest in experimental mineralogy during the last years because of their stability properties which make them potential index minerals and the formation of solid solutions with silicates (Brunet et al., 1998, Brunet & Chopin, 1995; Cemic & Schmid-Beurmann, 1995). However, for a successful application of calculated f to geobar- and/or geothermometry an internally consistent database for phosphate minerals is required.

This contribution focuses onto the sub-system $\text{Al}_2\text{O}_3\text{-MgO-P}_2\text{O}_5\text{-H}_2\text{O}$ of lazulite, $\text{MgAl}_2(\text{PO}_4)_2(\text{OH})_2$. Experimentally lazulite was found to share phase relations with berlinite, farringtonite, corundum, HD_2O and the phase MgAlPO_4O . Therefore knowledge of the thermochemical properties of MgAlPO_4O is a requisite to the extraction of those of lazulite from available experimental phase relation data (Cemic and Schmid-Beurmann, 1995). In contrast to previous results of Holland & Segnit (1980) DSC measurements in the range 25 to 700°C show a single transition: $\beta \Rightarrow 485^\circ\text{C} \Rightarrow \alpha$ with $\Delta H(\text{tr})$

EMPG IX

Ninth International Symposium on Experimental Mineralogy, Petrology and Geochemistry

= 0.65 kJ/mole instead of three (Holland & Segnit, 1980). HT X-Ray powder diffraction revealed a reduction of the molar volume by 1.5% at the transition temperature. Thermodynamic data for MgAlPO_4O were extracted from the reaction $\text{MgAlPO}_4\text{O} \rightleftharpoons \text{cor} + \text{farringtonite} + \text{berlinite}$ which was bracketed using an internally heated pressure vessel in the P-T range 0.4 to 0.8 GPa and 800 to 1100°C. In agreement with the calculated slope of the univariant curve of the phase transition HP-HT X-ray diffraction showed that under these conditions α - MgAlPO_4O is the stable modification. The following formation enthalpy and third-law entropy were retrieved for MgAlPO_4O taking heat capacities and thermal expansions of all reactants into account: $\Delta H(f)^\circ = -2387$ (kJ/mole) and $S^\circ = 111.5$ J/mole K.

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COMPOSITIONAL DEPENDENCY OF FERRIC IRON INCORPORATION IN SOLID SOLUTIONS OF THE LAZULITE-TYPE

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Iron bearing minerals with a variable $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio can be used as petrogenetic indicators for the oxygen fugacity. However, it was found experimentally that besides oxygen fugacity and to a lesser amount temperature this ratio can be strongly dependent on composition, e.g. in the case of synthetic (Mg,Fe)-foitites (Velickov & Abs-Wurmbach, 2000). Another interesting (Mg,Fe) dominated solid solution is the lazulite - scorzalite system the composition of which is ideally given as $(\text{Mg,Fe})\text{Al}_2(\text{PO}_4)_2(\text{OH})_2$. Natural lazulites are present as accessory phases in a variety of metamorphic environments (Pecora & Fahey, 1950). Under hydrothermal conditions the system forms a complete solid solution series which is mainly characterised by the exchange of Mg and Fe^{2+} on the octahedral Me^{2+} position of the Al-Me²⁺-Al trimers (Schmid-Beurmann et al., 1999). Fe^{3+} incorporation in synthetic lazulite - scorzalite solid solutions was investigated at 486°C and 0.3 GPa under the control of different solid state oxygen buffers like QFI-, Ni/NiO- and Hem/Mgt. With increasing oxygen fugacity the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio raises from 0.03 up to 0.06 in pure iron end member scorzalite. At constant oxygen fugacity this value was found to be significantly dependent on composition. Under the fugacity of the Ni/NiO buffer the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio increases from 0.04 in pure scorzalite up to 0.15 in the magnesium rich member $\text{Laz}_{0.875}\text{Sco}_{0.125}$. For the incorporation of Fe^{3+} into stoichiometric ferrous iron compounds a charge compensation mechanism is necessary. For an explanation a defect mechanism is formulated on the basis of the interpretation of the Mössbauer spectra of natural samples (Amthauer & Rossman, 1984). In their structure Fe^{3+} occupies the Me^{2+} as well as the Al^{3+} position. Such a mechanism is able to explain generally the hyperbolic increase of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio with decreasing Fe content.

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STRUCTURAL INFLUENCE OF WATER DISSOLUTION IN MELTS AND GLASSES ALONG THE JOIN REEDMERGNERITE-ALBITE

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In the present study we combined complementary spectroscopic techniques such as NMR, Raman and infrared spectroscopy in order to investigate the structural variations associated with B/Al substitution in a series of glasses along the join reedmergnerite-albite (NaBSi_3O_8 - $\text{NaAlSi}_3\text{O}_8$). Since natural B-rich melts are commonly associated with hydrous granitic magmas or an aqueous fluid phase, we focused in particular on the structural effects of water dissolution.

Glasses with five different compositions along the join reedmergnerite-albite (Rd-Ab) were investigated (Rd_{100} , $\text{Rd}_{75}\text{Ab}_{25}$, $\text{Rd}_{50}\text{Ab}_{50}$, $\text{Rd}_{25}\text{Ab}_{75}$ and Ab_{100} , in mol%). Hydrous glasses containing about 4 wt% water were synthesised at 2 kbar and 1000° C in TZM rapid quench autoclaves. Dry glasses were prepared at similar conditions (2 kbar, 1100° C, rapid quench) in order to minimize possible effects of different synthesis conditions on the glass structure. All glasses were analysed with IR, Raman and NMR spectroscopy.

The results show that B incorporates in the glasses as both, tetrahedral BO_4 and trigonal BO_3 groups. The B-speciation strongly depends on the anhydrous melt/glass composition and on the water content. Since ²⁷Al NMR data demonstrate that Al is only present in tetrahedral coordination, the presence of BO_3 groups indicates the presence of non-bridging oxygens. Only if all B-atoms were in tetrahedral coordination, the glasses would be fully polymerised. Near-infrared spectroscopy indicates important changes in the water speciation upon B-incorporation. The variations in the spectra indicate that for a constant total water content the concentration of structurally bonded hydroxyl groups increases while the concentration of molecular H_2O decreases with increasing B-content. Furthermore the spectral details may suggest the presence of B-OH complexes. However, the exact nature of such complexes cannot be deduced from the present data and needs further investigation.

EMPG IX

Ninth International Symposium on Experimental Mineralogy, Petrology and Geochemistry

EXPERIMENTAL OBSERVATION OF TRANSFORMATION PLASTICITY IN QUARTZ USING A HYDROTHERMAL DIAMOND-ANVIL CELL

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Transformation plasticity has long been proposed to be a significant mechanism for the localization of deformation in both Earth's crust and mantle. However, unequivocal experimental evidence of transformation plasticity in geologically relevant materials is still lacking. In this study, we used a hydrothermal diamond-anvil for in-situ deformation experiments of quartz containing synthetic water inclusions. During heating, a hydrostatic confining pressure was exerted on the quartz sample, which caused stress on the inclusion walls. The sample was monitored optically to determine the temperature of the α - β transition and PT conditions at which permanent deformation of the quartz around the fluid inclusions occurred. Plastic deformation of the quartz was recognized from permanent changes in inclusion shape and liquid-vapor homogenization temperature reflecting the change in inclusion density. Run durations were a few seconds to minutes at the maximum temperature and confining pressure. TEM images showed that deformation of the quartz around inclusions involved the motion of dislocations. Very high differences between confining and inclusion pressure above 400 MPa were required within the α -quartz stability field for the onset of plastic deformation. At the transition temperature, plastic deformation occurred at lower pressure differences (165 - 280 MPa). A pressure difference of 210 MPa was not large enough to cause plastic deformation in the β -quartz stability field at 760°C. However, the same inclusions deformed visibly at the transition temperature (710°C) at a pressure difference of 200 MPa after cooling of the sample along an isochore. These results indicate that there is a pronounced minimum of the creep strength of quartz at the α - β transition. Our experimental results imply that deformation in quartz-bearing shear zones can occur at much lower stresses than anticipated from existing flow laws and that fluid and melt inclusions in quartz can re-equilibrate at much shorter timescales than previously thought

IN-SITU DETERMINATION OF MINERAL SOLUBILITIES AT HIGH PRESSURES AND TEMPERATURES USING SYNCHROTRON RADIATION XRF

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Data for the solubility of minerals in aqueous fluids at the P-T conditions of the Earth's crust are fundamental in geochemistry because mineral-fluid equilibria control the behavior of elements during geological processes. One of the major difficulties associated with most available techniques for such studies is sampling of the fluid present at high temperatures and pressures. Here we present an experimental technique, which circumvents the sampling problem. This was achieved by determining the concentration of dissolved elements in a fluid

in-situ at high pressures and temperatures through the windows of a modified hydrothermal diamond-anvil cell using synchrotron radiation X-ray fluorescence. The cell was tested successfully to 800°C and 1.1 GPa, without reaching the upper P-T limits. The current experimental conditions permit analysis of elements with $Z > 18$ and concentrations above 10 ppm. The solubility of AgCl in water was determined as a function of pressure along two isotherms (300 and 455°C) to test internal consistency, accuracy, and reproducibility of the analyses. For standardless quantification, concentrations were calculated from the ratios of normalized peak areas of measured and Monte Carlo simulated spectra. These calculated concentrations show the expected increase in solubility with temperature, but are lower than literature data for the solubility of AgCl in water. This is probably not caused by sluggish dissolution of AgCl because the Ag concentration at 350 MPa and 300°C increased only insignificantly when the run duration was extended by 3000 s. Calibration against known solubility data along the liquid-vapor curve improved the accuracy. The reproducibility obtained from measurements at almost identical conditions was within 7%. Our preliminary data indicate that this in-situ technique has great potential for high P-T solubility studies because it can be applied to sparingly or incongruently soluble compounds and for studies of dissolution kinetics.

A 'ROCKING' MULTI-ANVIL APPARATUS: ELIMINATION OF COMPOSITIONAL SEGREGATION IN FLUID-RICH HIGH PRESSURE EXPERIMENTS

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Static experiments at high and ultra-high pressure conditions on equilibria involving hydrous phases and fluids suffer from an intrinsic problem: solubilities of solid components in high-pressure fluids are extreme and the gravitationally driven migration of the fluid to the top-end of the capsule causes chemical segregation. As a consequence, a strong compositional gradient results in the solid phase assemblages, zones with different mineral assemblages are frequently observed (e.g. Stalder & Ulmer, 2001). In addition, fluid migration and the dissolution processes are time- and fluid/rock ratio - dependent. Experimental determinations of high-pressure dehydration reactions from different groups are generally inconsistent (at least in the MgO-SiO₂-H₂O and in K-rich systems), part of this inconsistency might be attributed to chemical time-dependent segregation.

In order to overcome these problems we installed a rocking multi-anvil. A combined multi-anvil / piston-cylinder apparatus (total working range 1-20 GPa) has been mounted in such a way that it can be turned by 180 degrees while pressure and temperature are applied to the sample. We thus invert the gravitational field in our sample and the fluid is forced to migrate from one end of the capsule to the other. Preliminary experiments in the MSH system show that repeated turning results in a compositionally homogeneous environment thus avoiding the segregation problem. Continuous fluid migration also enhances reaction rates, which in future will allow the use of minimal fluid/rock ratios in the experimental charge.

EMPG IX

Ninth International Symposium on Experimental Mineralogy, Petrology and Geochemistry

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DISCONTINUOUS P-V-T BEHAVIOUR OF CORDIERITE BETWEEN 25 AND 800°C AND 0.0001- 1 GPa AND 0.0001- 1. GPa

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A reinvestigation of the thermal expansion up to 800°C at room temperature on Mg-cordierite from White Well/Australia and of the compression at room temperature up to 1 GPa on a MgFe-cordierite from Madagascar by X-ray diffractometry has been conducted.

The thermal expansion results confirm in a general way previous results (in Mirwald 1981a) exhibiting small positive thermal expansion for the basis parameters and a negative expansivity for the c-parameter. Detailed analysis, however, reveals clear discontinuities of anisotropic thermal expansion at 300°C and less pronounced at 550°C, leading to three temperature regions characterised by distinctly different trends of the thermal expansion coefficients what confirms earlier work (Mirwald, 1981a). The discontinuities are also manifested by intensity changes. The small volume changes which are mainly to be related with distortions within the vicinity of the Mg(Fe)-octahedron and the T1-tetrahedron, but not with changes in crystal symmetry, suggests isostructural transitions of displacive character within this framework silicate.

Discontinuous volume behaviour at 0.22±0.03 GPa had been suggested in a compression study by Mirwald et al. (1984). The present high-pressure X-ray study reveals closer details, a small change in the pressure-dependent evolution of both the lattice parameters and the unit-cell volume at 0.21 GPa. The apparent transition is very weak and shows the characteristics of a second-order transitions. Both polymorphs are of orthorhombic symmetry and compression behaviour is similar above and below the critical transition pressure with the a- and b-axis being approximately twice as compressible than the c-axis. These findings suggest very similar structural relationship between the two polymorphs with a displacive character for the structural transition.

The three transitions observed seem to fit in a system of discontinuous volume behaviour of cordierite lined out in a previous compression study at elevated P-T-conditions (Mirwald, 1981b).

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TETRAHEDRAL BORON IN OLENITE FROM THE TYPE LOCALITY: A CHEMICAL AND STRUCTURAL INVESTIGATION

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The recent discovery of tetrahedral boron with >1 ¹⁴B *apfu* in natural and synthetic olenite samples led to a reexamination of olenite from the type locality, Oleny, Kola, Russia. Contrary to the original publication from Sokolov et al. (1986) a single crystal structure analysis (*R* = 0.014) shows *ca.* 0.4 ¹⁴B *apfu* by site-refinement and chemical analysis. The optimized formula, calculated using chemical (EMPA and SIMS) and structural data is: (Na_{0.54}Ca_{0.02})_{Sum 0.56} (Al_{2.07}Li_{0.63}Mn_{0.09}Fe_{0.04})_{Sum 2.83} Al₆ (Si_{5.45}B_{0.40}Al_{0.14}) O₁₈ (BO₃)₃ (OH_{3.83}F_{0.16}O_{0.01}). The ideal formula was given by Sokolov et al. (1986) as Na_{1-x}Al₃Al₆B₃Si₆O₂₇(O,OH)₄. In contrast, the new investigation shows the *V* and *W* sites to be nearly fully occupied by (OH) with only small amounts of F and essentially no O. There is also a substantial amount of Li in the crystal investigated. The lattice constants of the studied material (*a* = 15.792(2), *c* = 7.0878(6) Å) are very similar to the parameters given by Gorskaya et al. (1982).

The chemical and structural detection of ¹⁴B in an olenite crystal from the type locality has important implications for future studies of the crystal chemistry of tourmaline group minerals. Substantial amounts of tetrahedral boron may be common in tourmalines with relatively high Al contents.

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HALIDE ION HYDRATION IN HYDROTHERMAL SOLUTIONS TO 350°C

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The interaction of dissolved species with solvent molecules is a fundamental feature defining the physical chemistry of aqueous electrolyte solutions. With increasing temperature to the critical point, the dielectric and transport properties of water change quite dramatically as changes in the hydrogen

EMPG IX

Ninth International Symposium on Experimental Mineralogy, Petrology and Geochemistry

bonding occur. The associated changes in ion hydration play an important role in determination the nature of oxygen and hydrogen isotope fractionations in high-temperature high-pressure aqueous systems. We have studied the interaction of iodide ion with solvent molecules using ultraviolet spectroscopy, X-ray absorption spectroscopy (EXAFS) and ab-initio/molecular dynamics techniques up to 350°C at equilibrium vapour pressures. The iodide-oxygen (water) distance was found to change from 3.55 to 3.63 Å from EXAFS measurement with increasing temperature from 25 to 350°C. This expansion of the hydration shell is consistent with the red-shifted ultraviolet charge-transfer-to-solvent spectra and the molecular dynamics simulation results.

PERMEABILITY OF THE CONTINENTAL CRUST: IMPLICATIONS OF EXPERIMENTAL DATA

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Permeability is an important geochemical and geophysical property controlling the migration of fluids which, in turn, play a fundamental role in mass and heat transfer within the crust as well as crust rheology. Field permeability measurements were conducted on sand, sandy loam, loam and humus strata (Orlovka ecologic testing area, Eastern Transbaikalia) at ambient pressure and temperature. Laboratory permeability measurements were conducted on granitoid, gneiss and amphibolite samples from Kazakhstan and Kola super-deep borehole at T = 20-600°C and P_{eff} up to 200 MPa. The analytical expression for the permeability (k, m²) – depth (H, km) trend (15 samples, 229 experimental points) is given by $\log k = -12.55 - 3.374 H^{0.2093}$. At the 90% prediction interval the permeability decreases from $2.82 \times 10^{-13 \pm 1.8}$ m² at the surface to $1.67 \times 10^{-20 \pm 1.5}$ m² at the base of the crust. These permeability values refer to the crust under isotropic stress conditions ($\sigma_x = \sigma_y = \sigma_z$) in the state of mechanical ($d\epsilon_x = d\epsilon_y = d\epsilon_z = 0$) and chemical ($\Delta G = \min$) equilibrium. The experimental results are compared to the permeability estimates from the oxygen isotope front propagation [Dipple & Ferry, 1992] and the hydrothermal flow rate in metamorphic systems [Manning & Ingebritsen, 1999]. This work was financially supported by the RFFR grant 01-05-64531.

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STUDY OF THE HAWAITE MELTING DIAGRAM AT PH₂O=600 bar WHILE USING SEED TECHNIQUE

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Seed technique is an experimental method used in some instances for the equilibrium diagram determination. Observation of the reaction zone on the border of the large plagioclase crystals was used in the study of granite melting diagram [1], in the simple systems mineral solubility relates to its liquidus. In the current study we use diopside, forsterite and plagioclase seeds to define liquidus or metastable liquidus extension (metastable equilibrium of the single given phase with the melt) temperature of the correspondent phases. Experiments have been carried out on IHGV at the parameter values close to the levels assumed for the intermediate storage magma chamber at the Mt. Etna volcano PH₂O=600 bar, fO₂ about Ni-NiO. Water solubility for these conditions is about 2.5 wt.%. We observe switch from the seed dissolution to the seed overgrowth in the experiments with duration 10-30 min. Liquidus temperature of the clinopyroxene is found to be 1100±5°C and olivine 1120±5°C. These values fit with experimental uncertainty to the estimates found with program MELTS [2] for the given melt composition (Ol- 1120±8, Cpx- 1105±2, estimates range connects with possible melt composition and fO₂ variations). Experimentally determined metastable liquidus extension for the plagioclase is 1060±5 (liquidus at 1045±5°C) exceeding on 20°C estimate made with MELTS. Clinopyroxen growth rate at DT=25-30°C for the elongated crystals consists 2-3 10⁻⁵ cm/s while for the smooth overgrowth it is order of magnitude lower 2-3 10⁻⁶ cm/s. Registered Al₂O₃ content in clinopyroxen at small undercoolings is 4-6.5 wt.% very close to the level predicted with MELTS. Experimental estimates of the clinopyroxen growth rate are in accordance with the scenario of the crystallization due to degassing at the magma uplift from the shallow (depth about 2 km) reservoir to the surface. Clinopyroxen can reach maximum size 0.8-0.9 mm just around maximum size found by CSD measurements in Mt. Etna lavas. This study was supported with RFFR grant #00-05-65371.

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EMPG IX

Ninth International Symposium on Experimental Mineralogy, Petrology and Geochemistry

CARBORN NANOTUBES AND FULLERENE-LIKE PHASE FORMATION AT THE METAMORPHIC PARAMETERS

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At low temperatures and pressures (700-750°C and 5 kbar) from the methane and hydrocarbon gases graphite, fullerite structures and carborn nanotubes were synthesised. Fullerite formations have overall forms and multyplies structure. Nanotubes has length up to 1 µm, diameter nearly 600 Å and diameter of the channel nearly 40 Å. Microdiffraction were provided for these structures. As a result we can conclude that rare phases of the carborn - fullerene-like structutes and nanotubes which are known for very high temperatures processes could be formed at the metamorphic P-T parameters.

SYNTHESIS OF MORDENITE SINGLE CRYSTALS FOR DYE INCORPORATION

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Natural antenna systems in plants where the sunlight is transformed into chemical energy are well known. This principle of energy transfer can also be reproduced by artificial antenna systems using zeolites used as hosts for supramolecular organization of dyes. Dye molecules loaded into zeolite channels mimic the natural function of chlorophyll in plants. The incorporation of the organic dye molecules is dependent on the aperture of the zeolite channels. The orientation of the molecule in the channel is determined by the shape and size of the dye and the zeolite channels. Very little is known about geometrical arrangement of the dyes in these channels. The exact position of the chromophores in the zeolite structure may provide better understanding how the antenna systems work and how the energy transfer can be improved. A suitable method to analyze the modified zeolite structure is single-crystal diffractometry applying synchrotron radiation.

Mordenite ($\text{Na}_8(\text{Si}_{40}\text{Al}_8\text{O}_{96})(\text{H}_2\text{O})_{24}$, space group Cmc₂m, was chosen as an ideal candidate for dye incorporation. The large ellipsoidal 12-membered ring channels along [001] with an aperture of $7.0 \cdot 6.5$ Å are tailor-made for incorporation of small organic dyes. The anisotropic shape of the channel cross-section limits disorder of the enclosed molecules.

Different hydrothermal-synthesis methods were applied to obtain suitable single crystals. The most important aspects during the synthesis were control of size, morphology, and quality of the single-crystals. Mordenite single crystals up to 180 µm in length with different morphology (platy, prismatic) were synthesized. Some of these crystals were loaded in gas phase with the organic dye fluorenone ($\text{C}_{13}\text{H}_8\text{O}$). IR spectra were collected to confirm dye incorporation into the mordenite structure. However, only small amounts of the dye could be loaded during the first trials. For successful single-crystal diffractometry, the filling procedure has to be improved.

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EFFECTS OF HYDRATION ON THE CRYSTAL STRUCTURE OF OLIVINE

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The effects of hydration on the crystal structure of olivine have been investigated by means of X-ray single crystal structure refinements on a series of samples synthesized at elevated temperatures and pressures. The samples were synthesized in the multianvil press laboratory at BGI from powdered mixtures of olivine, brucite, orthopyroxene, and magnetite. Under hydrous conditions, the olivine to wadsleyite transformation occurs at about 1 GPa lower pressure than in the dry system. Preliminary IR spectroscopic data indicate that the samples synthesized at contain up to about 1500 ppm by weight H_2O as hydroxyl. High precision X-ray single crystal structure determinations were conducted on four of the synthetic hydrous samples together with two natural and one synthetic anhydrous samples for comparison. The hydrous olivines indicate that the unit cell expands by approximately 0.17% relative to the anhydrous equivalent. This is sufficient to reduce the bulk modulus and seismic velocities significantly. Crystal structure refinements indicate that the principal hydration mechanism is by M2 vacancy based on observed scattering deficiency coupled with volume expansion of the M2 coordination polyhedron.

PYROGENIC TRANSFORMATION OF PELITES

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High-temperature transformation of pelitic rocks during prolonged combustion metamorphic events was studied on the example of the matter from burned coal dumps (the Urals, Russia). The parent rocks are mainly mudstones containing muscovite-illite, quartz with small amounts of montmorillonite, kaolinite, chlorite, and diaspore. At the initial stage of

EMPG IX

Ninth International Symposium on Experimental Mineralogy, Petrology and Geochemistry

heating ($T=600-700^{\circ}\text{C}$) decomposition of layer silicates involving their dehydroxylation (H_2O and Na loss) and amorphization is the principal process. Amorphous phase dominates in the annealing products, whereas crystalline phases are represented only by quartz, mullite and thermally altered muscovite. With increasing temperature up to 900°C and prolonging the heating processes of sintering and crystal growth occurred in amorphous matrix. Crystalline phases are quartz, mullite, hercynite, and cordierite. The amount of cordierite is inversely related to hercynite ones. This result allows to predict cordierite generation by solid-state reaction: Herc + SiO_2 (amorph.) = Cord. Hercynite is intermediate short-lived phase petering during the prolonged heat treatment.

The melting of dehydrated and amorphized substrate starts below 900°C . The first partial melts have a near constant composition which is controlled by the eutectic of mudstones. High-temperature clinkers ($T=900 - 1250^{\circ}\text{C}$) are largely composed of Al-K high-silica glasses, corresponding in their composition to S-granites. Minerals are represented by K-bearing cordierite, tridymite, mullite, and magnetite, which crystallized during cooling. Thus during the dimensioned coal conflagrations in dumps primary mineral assemblages were transformed into anhydrous silicates, oxides and glasses.

Principal feature of combustion metamorphic reconstruction of sedimentary matter is the amorphization phenomenon. Within several years mudstones are baked at the temperature $500 - 700^{\circ}\text{C}$, which is sufficient for dehydroxylation and amorphization of layer silicates. As temperature rose, not crystalline phases, but a fine-grained admixture of amorphous products were melted. This feature is a key to understanding the similarity between the processes of pyrogenic transformations of pelites and industrial ceramics production.

EXPERIMENTAL CONSTRAINTS ON MAGMA FRAGMENTATION DURING THE SUMMER 2001 FLANK ERUPTION OF MT. ETNA (ITALY)

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The experimental fragmentation of magma provides insights into mechanisms inaccessible to field-geology, such as the brittle fragmentation of magma due to rapid decompression. This mechanism plays a role in a variety of explosive eruptions, and is believed to be responsible for the pulsated ash explosions that occurred in the last explosive phase (1-5 Aug.) of the 2001 flank eruption of Mt. Etna (Italy). We are using a shock-tube-like fragmentation bomb to define the overpressure range responsible for the magma fragmentation. The fragmentation threshold is measured on samples (60 mm long, 24 mm diameter) drilled from porphyritic, micro- to crypto-crystalline, trachybasaltic bombs from the last explosive phase. These are believed to represent the pre-fragmented magma.

During the experiments the samples are loaded into an autoclave that is taken to high temperature (up to 900°C) and high pressure (up to 50 MPa). The autoclave is separated from a tank at ambient temperature and pressure by a set of diaphragms. The pressure in the autoclave is increased and rapid decom-

pression is triggered by the bursting of the diaphragms. Starting the experiments far below the expected threshold, the experimental pressure is raised stepwise up to the fragmentation threshold.

Pressure drops of 7.5-20 MPa caused fragmentation of samples with total porosities ranging from 4-21% and a variety of pore-textures. There is an inverse correlation between porosity and fragmentation threshold. Temperature changes on the order of 100°C do not have a major effect on the threshold. Future work will include comparison of the grain size, morphology and petrology of the experimental and natural pyroclasts. This will further define the physical constraints of the eruption mechanism.

DIAMOND CRYSTALLIZATION IN CARBONATE-SILICATE MELTS OF DIAMOND-BEARING ROCKS OF THE KOKCHETAV MASSIF (EXPERIMENT AT 5.5 - 7.5 GPa)

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Experimental modeling of diamonds genesis of metamorphic complexes (Kokchetav, Kazakhstan; Dabie Shan, China) was executed. Carbonate-silicate dolomite-garnet-clinopyroxene rock from the Kumdy-Kol, Kokchetav deposit was used in experiments at high pressures. This type of the rocks differs by the extreme contents of diamonds (2000 carat/ton). Both tectonic and mineralogical data testify genesis of diamond-bearing rocks of the metamorphic complexes at the mantle conditions under high pressure (Perchuk et al, 1995).

Diamond synthesis at pressures 5.5 - 7.5 GPa was realized in dolomite-garnet-clinopyroxene melts of the rock from Kumdy-Kol. The melts were supersaturated with carbon of graphite from a starting mixture. Experimental PT - diagram of diamond formation is constructed. Diamond crystallization occurs both at spontaneous nucleation in first 1 - 2 minutes of exposition and at seeded growth. The diamonds crystallize as octahedron single crystals with smooth facets, spinel twins, aggregates by the sizes up to 100 μm . High pressure generation of garnets and clinopyroxenes is formed in the same melts as diamonds crystallize. These results support the carbonatite model of diamond genesis in the mantle, justified by experiments on diamond synthesis in the substances of primary fluid - carbonatite inclusions in diamonds from kimberlites (Litvin & Zharikov, 2000)

Experimental evidence of high efficiency of the carbonate-silicate melts as a parental medium for natural diamond genesis is found. In addition to the mineralogical studies (Perchuk et al, 1995), experimental data indicate that carbonate-silicate melts could be both primary medium of diamond formation in the mantle and diamond carrier to the Earth's crust. Support: grant 01-05-64775 of FRBR.

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EMPG IX

Ninth International Symposium on Experimental Mineralogy, Petrology and Geochemistry

HYDROGEN INCORPORATION IN ENSTATITE

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Orthopyroxene is the second most abundant mineral in the Earth's upper mantle. Although nominally anhydrous, it is able to dissolve traces of OH as point defects and might be a major host for water in the Earth's mantle. The aim of this study is to investigate the incorporation mechanism of hydrogen in enstatite and to reveal potential lattice sites for hydrogen in the crystal.

A series of enstatite crystals containing between 0 and 1000 ppm Al has been synthesized at 25 kbar under hydrous conditions. Crystals with different Al-content were oriented in a thermoplastic resin according to their crystallographic axes, and ground and polished on both sides. IR-spectra of each sample were recorded in the wavelength range of 1000 and 4000 cm^{-1} , and the water contents were determined.

All spectra show several absorption bands in the region between 3000 and 3600 cm^{-1} , which are assigned to O-H stretching modes; the strongest absorption occurs when γ is parallel to the electric field vector of the incident light. Pure enstatite only exhibits two major O-H absorption bands at 3070 and 3360 cm^{-1} , whereas in Al-bearing samples additional peaks above 3400 cm^{-1} are present. Furthermore the absorption band at 3360 cm^{-1} is split into three peaks, the main peak shrinking on the costs of two sidebands at approximately 3330 and 3380 cm^{-1} with increasing Al-content. The observations are consistent with a model, where hydrogen in pure, Al-free enstatite is linked to the oxygen atoms O(3A) and O(3B), which are located at SiO_4 -tetrahedron faces pointing towards the cavity between two M2-positions along the crystallographic b-axis. In Al-bearing samples additional water is mainly incorporated between the oxygen atoms O(2A) - O(1A) and O(2B)-O(1B), i.e. at the M1 and M2 polyhedra.

AN EXPERIMENTAL STUDY OF SILVER TRANSPORT IN HYDROTHERMAL SOLUTIONS

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A knowledge of the stability of aqueous silver(I) complexes in hydrothermal solutions is essential for quantitative interpretation of the transport and deposition mechanisms of silver by hydrothermal fluids in the earth's crust. High temperature experimentally obtained data exist for many aqueous silver(I) complexes including chloride, hydroxy, hydroxychloro, carbonate and hydroxycarbonate complexes. Less is known about the stability and stoichiometry of silver(I) sulphide complexes in aqueous solutions at high temperatures and pressures. The solubility of well characterised silver sulphide (argentite/acanthite) was measured in dilute sulphide solution to 400°C at vapour saturation pressure and 500 bar. The experiments were carried out in a flow-through autoclave, connected to an HPLC pump, titanium-sampling loop and a back-pressure regulator on line. Samples for silver determination were collected via the titanium-sampling loop at experimental

temperatures and pressures. The solubilities, measured as total dissolved silver, were in the range $1.0\text{E-}7$ to $1.30\text{E-}4$ mol kg^{-1} , in solutions of total reduced sulphur between 0.007 and 0.176 mol kg^{-1} and pH(T,P) of 3.7 to 12.7. A non-linear least squares treatment of the data demonstrate that silver sulphide dissolves in aqueous sulphide solutions to form $\text{AgHS}(\text{aq})$, $\text{Ag}(\text{HS})_2^-$ and $\text{Ag}_2\text{S}(\text{HS})_2^{2-}$ complexes dominating in acidic, neutral and alkaline solutions, respectively. The solubility constants and the cumulative and stepwise formation constants for the respective species have been calculated to 400°C. The complex formation at 25°C is characterised by exothermic enthalpy and a small entropy indicating the chemical bonds formed between Ag^+ and HS^- are predominantly covalent. At higher temperatures the formations reactions become more endothermic with large positive entropies, indicating of greater electrostatic interaction. Sulphide complexes will play an important role in the transport and deposition of silver by hydrothermal fluids in the crust.

EXPERIMENTAL MODELLING OF THE SILICATE-CARBONATE LIQUID IMMISCIBILITY

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Silicate-carbonate liquid immiscibility was experimentally studied in a high gas pressure vessel at $T=1100$ and 1250°C and $P=2$ kbar to modelling the separation of carbonatite melt from silicate magma. The splitting of initial melts into two liquids (silicate and carbonate) was determined. The distribution of REE (La, Ce, Y), Nb, Ta, Ba, Sr between immiscible phases was investigated.

At $T=1100^\circ\text{C}$ the dependence of the coefficient of distribution of REE on the initial composition of the system is determined: in alkaline silicate-carbonate systems REE are accumulated in carbonate phases, but in lime ones they are redistributed in favour of silicate liquid. These data make it possible to conclude about the formation of REE-deposits exclusively with respect to alkaline (agpaitic) magmatism. The dependence of this coefficient on the temperature is also determined: the increase of temperature from 1100 to 1250°C results in redistribution of REE in favour of silicate phase. Nb and Ta are mostly concentrated in silicate melt, but Ba and Sr are accumulated in carbonate phase.

Inhomogeneity of the obtained carbonate liquids, manifesting itself in the division of carbonate phase into alkaline (mostly sodium) and alkaline-lime (mostly calcium) facies is pointed out. This type of splitting probably played a certain part in the formation of carbonatite intrusions of various types and their ore-bearing.

The effect of salt additions (phosphate, fluoride, chloride, sulphate) on silicate-carbonate layering of melts and distribution of ore elements between immiscible phases has been investigated. Experimental results illustrate positive role of phosphorus and fluorine and negative role of chlorine on the extraction of REE by salt melts. This fact can explain usual presence of apatite mineralization at the REE-deposits of carbonatite type.

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