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ALUMINUM POSITION IN SYNTHETIC Rb-FELDSPAR AS DETERMINED BY X-RAY PHOTOELECTRON SPECTROSCOPY

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Aluminums occupying two kinds of structural sites of synthetic Rb-feldspars have been detected by Al 2 p X-ray photoelectron spectra. Chemical compositions and properties of the synthetic Rb-feldspars were characterized using classical methods: electron microprobe analysis, X-ray powder diffraction analysis and Fourier transform infrared microspectroscopy. Resultantly small amounts of H₂O molecule and of excess Si and Al have been detected for all single crystals of the Rb-feldspars. Moreover the quantities of excess-Al are on average 0.044 apfu and negatively correlated with those of Rb. Inasmuch as this negative correlation suggests the presence of excess-Al occupying non-tetrahedral sites of the feldspar structures, incorporation of the “Al(Al₃Si)O₈ molecule” into the Rb-feldspars has led to presentation of appropriate endmembers for the unusual chemical compositions. Thus the representative EPMA allow the present Rb-feldspar to be identified as the non-stoichiometric feldspar with excess of Si and Al, resulting in a unit formula of (Rb_{0.831} Al_{0.125} Al_{0.044}) Al_{0.963} Si_{3.037} O₈, where the site is occupied by H₂O molecule. In order to confirm excess-Al occupying the extra-framework sites of the feldspar structure, the effect of Al-Si ordering on Al 2 p X-ray photoelectron spectra of feldspars has been examined, using a monochromatized AlK α X-ray source, in comparison with the Rb-feldspars and several feldspar minerals. Al 2 p XPS signals of the Rb-feldspars reveal appreciably higher energy than any others of feldspars (sanidine, orthoclase, microcline and low albite) and higher one than that of bicchulite [Ca₂Al₂SiO₆(OH)₂], one of the exceptional minerals for the “aluminum avoidance rule”. Since the present Rb-feldspar is generally similar in Al-Si disordering to sanidine, shift of the Al 2 p X-ray photoelectron spectra toward the higher energy side provides a reasonable explanation for coexistence of the Al at extra-framework sites with the tetrahedral Al-O-Al linkage within the present Rb-feldspar.

CRYSTAL CHEMICAL CONTROLS ON RARE-EARTH-ELEMENT PARTITIONING BETWEEN EPIDOTE-GROUP MINERALS AND MELTS

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We have combined structural and physical data for epidote-group minerals (allanite, epidote s.s., clinozoisite and zoisite) with the elastic strain model of Blundy and Wood (1994) in order to qualitatively predict the changes of REE+Y mineral/liquid partitioning pattern with changing crystal structure. In addition, we present the first experimental data for partitioning of REE+Y between zoisite and hydrous silicate melt. Comparison of the predicted partitioning pattern with our new experimental zoisite/melt partitioning data and natural allanite/melt partitioning data suggests that REE+Y are preferentially incorporated into the A2 site of epidote-group minerals and that mineral/melt partitioning patterns are mainly controlled by the size and shape of the A2 site of these minerals. As a result all epidote-group minerals are expected to strongly fractionate the LREE from the HREE in mineral-melt systems. The moderately compatible behaviour of LREE and MREE in zoisite suggests that melts generated in the presence of zoisite are highly LREE and MREE depleted. In contrast, the available data for partitioning of REE between epidote-group minerals and fluids show no or little agreement with predicted REE partitioning pattern and suggest that fluid composition and oxidation state are likely to have a strong effect on the REE partitioning pattern. However, both mineral/melt and mineral/fluid partitioning data reveals that charge balancing mechanisms may exert important controls on absolute D_{REE+Y} values for epidote-group minerals. The elastic properties of the allanite and zoisite A2 site, obtained by fitting our new and existing mineral/melt partitioning data for trivalent cations to the elastic strain model of Blundy and Wood (1994), indicate that the bulk elastic properties of epidote-group minerals are dominantly controlled by the large cation sites.

Blundy JD, Wood BJ, *Nature*, **372**, 452-454, (1994).

DEFECT MICROSTRUCTURES AS A GENETIC FINGERPRINT OF DIAMONDS

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Diamonds occur in a great variety of natural environments such as ultra-high pressure metamorphic belts, kimberlite pipes, impact craters, and meteorites. These different occurrences of

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diamonds reflect formation by various mechanisms, as diverse as crystallization from melt, vapour condensation, and solid-state transformation. Therefore it seemed possible that the defect microstructures of diamonds provide a fingerprint to their genesis. To test this hypothesis, we have conducted a TEM study on diamonds from the following sources: (i) metamorphic diamonds from Kokchetav and Erzgebirge, (ii) impact diamonds from Ries and Popigai craters, and (iii) kimberlitic diamonds from various pipes. The microstructure of meteoritic diamonds was extensively studied by Dalton et al. (1996).

The metamorphic diamonds observed occur primarily as inclusions in the container mineral garnet. Particularly the diamonds from Erzgebirge are surrounded by other minerals such as intercalated sheet silicates, apatite, anatase, quartz, and plagioclase. The diamonds usually exhibit octahedral faces, occasionally with skeletal morphology. Most importantly, the microstructure of these diamonds is absolutely defect-free. This contrasts with observations on diamonds from all other sources.

Kimberlite diamonds usually contain dislocations, especially in the presence of tiny inclusions which possibly act as dislocation sources during the rapid ascent within a pipe. Impact diamonds are pervaded by numerous twin bands. These bands are inherited from precursor graphite that, prior to transformation, was deformed by shock compression. Presolar diamonds occurring as inclusions in meteorites contain interconnected stacking faults and microtwins (Dalton et al., 1996), which indicates condensation from vapour.

In conclusion, the present microstructural comparison of diamonds from various environments reveals structural and textural characteristics indicative of the geological process that produced them. Detailed TEM studies may thus provide profound insights into the origin of natural diamonds, even if the diamonds occur as loose grains in placer deposits.

Daulton TL et al., *Geochim. Cosmochim. Acta*, **60**, 4853-4872, (1996).

STABILITY OF PICOILMENITE FROM KIMBERLITE (PHYSICO-CHEMICAL MODEL AND EXPERIMENT)

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Stability of metastable picroilmenite in case of varying P-T parameters and the fluid regime is discussed. Method of physico-chemical modeling of geochemical systems (Karpov et al., 1997) and experimental study of retrogressive metasomatism are used for this purpose. Stability of picroilmenite under equilibrium conditions in the temperature range from 400 to 1000°C and pressure from 1 to 50 kbar was considered. Fluid phase was given by water and carbonic acid in proportion H₂O/CO₂ -39.08, 3.9 and 2 in amounts from 1.5 to 3-weight%. The modeling of the picroilmenite stability demonstrated its stability in hydrous systems. Decomposition of picroilmenite in the presence of carbonic acid into carbonate-rutile or carbonate-rutile-perovskite (with CaO in the system) associations is noted. Under conditions of higher oxygen fugacity and CO₂ content in fluid phase the picroilmenite serves as a pecu-

liar buffer in conservation of diamond. The range of diamond stability in kimberlite system significantly increases at expense of redox reactions in picroilmenite structure (variation of FeO/Fe₂O₃ and Mg/Fe ratios) and binding excessive CO₂ into carbonate. Experimentally, chemical zoning expressed in obvious change of its composition from the center of grain to its periphery forms during reaction of substitution of picroilmenite at T=800°C and P= 2000 atm and the fluid of C-O-H system: 1) decrease of TiO₂ and Fe⁺⁺, 2) sharp increase of Fe⁺⁺⁺ oxide and oxides of Al, Mg and Cr. Change of oxygen regime of kelyphitization is following by oxidation from FeO to Fe₂O₃ which may enter into structure of modified ilmenite or forms its own titanomagnetite phase. The work was supported by the RFBR, grant # 01-05-65269

OXYGEN FUGACITY BUFFERING WITH CO₂/H₂ MIXTURES BETWEEN 700° AND 1200°C

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Gas mixing techniques are among the most versatile methods for the control of oxygen fugacity at low pressure. CO₂/H₂, CO/CO₂ and H₂/H₂O mixtures can reliably buffer *f*O₂ above 1200°C, whereas below this temperature deviations from calculated fugacities are frequent. These differences are caused by incomplete equilibration within the gas phase, thermal partitioning of the reactants, inaccuracies in flow and temperature control, differences in experimental conditions, configuration factors, etc.

Performances are strongly influenced by the experimental set-up and discrepancies between individual authors are often due to the lack of standardization: careful calibrations which take in consideration all parameters affecting the fugacity in the T-*f*O₂ regime of interest are crucial to properly control the run conditions in any furnace.

Extended calibration work was carried out on a classical gas-mixing furnace (GMF) and on a High-Temperature Diffraction (HTD) camera which was equipped with a CO₂/H₂ mixing system in order to do *in-situ* high temperature analysis under controlled atmosphere.

The iron-wüstite buffer was used as calibration couple: for the GMF quenched samples were analyzed by Raman Spectroscopy and XRD, while the HT-diffractometer was calibrated directly monitoring the buffer reaction: in both cases the observed fugacities are more reduced than expected and present the largest deviations at 800°C.

To verify if these results could be extrapolated in a different fugacity range, we calibrated the wüstite-magnetite buffer too: the deviations are comparable in the HTD but significantly larger in the GMF.

The effects of flow reduction and of the presence of platinum as catalyst were evaluated, both to investigate the crossed influence of slow kinetics and thermal segregation, and to try to minimize the deviations: the kinetic problem is predominant and the catalytic solution is especially effective in the GMF.

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For the furnace set-up, the influence of the use of a sample container was tested. Interestingly, the atmosphere within a crucible is significantly more oxidized than in the free gas stream and therefore gets closer to the thermodynamically expected one.

TOWARDS A THERMODYNAMIC DATABASE FOR PHOSPHATE MINERALS: ELASTIC PROPERTIES OF MG-PHOSPHATES AND PHASE RELATIONS IN THE SYSTEM $MgO-Al_2O_3-P_2O_5-SiO_2-H_2O$

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Although less common in nature than other phosphates like apatite, Mg-phosphates are useful petrological indicators owing to their numerous polymorphic relations. Despite the wide range of other applications (in the cement and fertilizer industry, in medicine), very few thermodynamic data are available, even in as simple a system as $MgO-P_2O_5-H_2O$: calorimetric data exist only for farringtonite ($Mg_3(PO_4)_2$), a low-pressure anhydrous Mg-phosphate (Oetting and McDonald, 1963). On the other hand, the phase relations between farringtonite and its high-pressure polymorph Mg-sarcopside, and between the Mg_2PO_4OH polymorphs (ϵ - Mg_2PO_4OH , holtedahlite, althausite and hydroxywagnerite) as well as the stability field of phospho-ellenbergerite ($(Mg_{1-x}, [X]_x)_2Mg_{12}P_8O_{38}H_{8+4x}$, x about 0.1) have already been experimentally studied (Brunet et al., 1998). However, because of the lack of sufficient 'anchor' phases with well-defined thermodynamic properties, no thermodynamic data could be extracted for Mg-phosphates in the system $MgO-P_2O_5-H_2O$.

Through consideration of silica or alumina as additional components, we were able to study two reactions involving three known solid phases and a single 'unknown' phosphate: the reaction P-ellenbergerite + quartz = Mg-sarcopside + talc + H_2O has been bracketed between 575 and 600°C near 9 kbar and between 18 and 20 kbar at 775°C, and althausite + corundum = Mg-sarcopside + spinel + H_2O between 800 and 820°C near 9 kbar. Combined and tested for compatibility with existing phase-equilibrium data, they allow extraction of thermodynamic properties for most Mg-phosphates. Actually, a more rigorous treatment requires consideration of elastic properties. Therefore, compressibilities and thermal expansions of wagnerite, farringtonite, Mg-sarcopside and P-ellenbergerite were determined up to 55 kbar, 900°C using a multi-anvil apparatus at the HASYLAB-DESY synchrotron facility (Hamburg).

Extension of this system to additional components involving well-characterised mineral phases like apatite - $Ca_5(PO_4)_3OH$, berlinite - $AlPO_4$, or lazulite - $MgAl_2(PO_4)_2(OH)_2$ (Schmid-Beurmann & Brunet, this meeting) provides us with a thermodynamic database, allowing the calculation of phase relations for most phosphates in metamorphic rocks.

Oetting FL & McDonald RA, *J. Phys. Chem.*, **67**, 2737-2743, (1963).

Brunet F, Chopin C, Seifert F, *Contrib. Mineral. Petrol.*, **131**, 54-70, (1998).

THE T-X_{ps} DEPENDENCY OF THE ISOSYMMETRIC DISPLACIVE PHASE TRANSITION IN SYNTHETIC Fe³⁺-Al ZOISITE: A POWDER X-RAY DIFFRACTION AND TEMPERATURE DEPENDENT INFRARED SPECTROSCOPY STUDY

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Rietveld refinements based on powder X-ray diffraction patterns of synthetic Fe³⁺-Al zoisite [$Ca_xAl_2Al_{1-x}Fe^{3+}_xSi_3O_{11}(O/OH)$] in the compositional range of 0.0 - 0.14 X_{ps} [$X_{ps} = Fe^{3+}/(Fe^{3+}+Al-2)$] yield two zoisite modifications (I and II) with the following lattice parameters: zoisite I: a [Å] = $-3.72 \cdot 10^{-2} X_{ps} + 16.1913$; b [Å] = $6.43 \cdot 10^{-2} X_{ps} + 5.5488$; c [Å] = $3.43 \cdot 10^{-2} X_{ps} + 10.0320$; V [Å³] = $11.4 \cdot X_{ps} + 901.3$, and zoisite II: a [Å] = $-8.26 \cdot 10^{-2} X_{ps} + 16.2061$; b [Å] = $8.14 \cdot 10^{-2} X_{ps} + 5.5486$; c [Å] = $1.18 \cdot 10^{-1} X_{ps} + 10.0263$; V [Å³] = $19.3 \cdot X_{ps} + 901.6$. The lattice parameters show discontinuities at $X_{ps} = 0.05$ between zoisite I and II. The Rietveld refinements suggest that the phase transition between zoisite I and II is isosymmetric and displacive. The dependency of this phase transition on temperature and composition has been determined by temperature dependent infrared spectroscopy. Spectra were recorded in 20°C-steps in the temperature interval -170 to 250°C. Because the zoisite II structure is more flexible than the zoisite I structure, the positions of the IR-bands display a stronger temperature dependency of zoisite II than of zoisite I and the transition from zoisite I to II is mirrored by discontinuities in band-position in response to temperature. These discontinuities between zoisite I and II are best displayed by the OH-band at approx. 3150 cm⁻¹ and by two bands at approx. 909 and 950 cm⁻¹. The data indicate that zoisite II is the high temperature form and that the critical temperature of the phase transition is negatively correlated with the iron content in zoisite according to the equation $T_c = 65 - 900 \cdot X_{ps}$ [°C], with $\Delta T_c = \pm 35^\circ C$.

MELTING OF PERIDOTITE UNDER LOWER MANTLE CONDITIONS

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Peridotite phase relations and mineral-melt partitioning along the mantle solidus are required in order to understand the earliest differentiation of the Earth's mantle, which may have occurred during the crystallization of a magma ocean. In this study melting experiments are being performed on synthetic mantle peridotite doped with a selection of 21 trace elements to determine melting temperatures and partitioning relations between crystals and melt at conditions applicable to the lower mantle. Melting experiments are being performed in the 22-28 GPa pressure range in a multi-anvil apparatus using 10/4 and 7/3 (octahedral edge length/anvil truncation length in mm) pressure cell configurations with LaCrO₃ heaters and axially inserted WRe thermocouples. The phases are analyzed by scan-

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ning electron microscopy and electron microprobe. Several peridotite compositions with differing degrees of fertility have been examined.

We have performed experimental runs in both Re and graphite capsules to investigate the influence of oxygen fugacity on the phase relations of minerals such as magnesiowüstite, perovskite and garnet, which can dissolve significant amounts of ferric iron. Experiments performed in Re capsules and in graphite, (which imposes a lower fO_2 than Re), yielded different coexisting phases under identical subsolidus conditions of 23 GPa and 2200°C. Garnet, magnesiowüstite and magnesium silicate perovskite were observed in the Re capsule whereas no evidence was found for perovskite in the graphite capsule which has transformed to diamond during the run. This implies that there may be a perovskite stabilizing effect resulting from higher fO_2 .

STRUCTURAL CHANGES IN CALCINED NH_4 -CHABAZITE

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The hydrogen form of natural chabazite obtained through deammoniation of NH_4 -chabazite at calcination up to 400°C is characterized by acid catalytic properties (Beyer et al., 1977). To investigate the overall structure persistence during formation of H-chabazite the samples of NH_4 -exchanged natural chabazite $Ca_{1.63}Na_{0.16}K_{0.12}[Al_{3.77}Si_{8.26}O_{24}]12.75H_2O$ (Khilok River, Transbaikalia) calcined under vacuum shallow-bed conditions at 100°, 250°, and 400°C and rehydrated in air were studied by X-ray diffractometry and IR spectroscopy. The intensity of X-ray diffraction peaks decreases at 250° when deammoniation starts to proceed, and slight amorphization occurs at 400° when the almost fully protonated structure is formed. The parameters of rhombohedral unit cell slightly decrease at 250°; at 400° the contraction of the unit cell volume achieves 1.8% compared to the initial NH_4 -chabazite. The extent of the volume contraction is comparable with that observed in natural chabazites when passing from medium to high-silica varieties (Passaglia 1975). The changes in the framework IR spectrum are more noticeable compared to structural data. The high-frequency shift of the main framework T-O stretching mode near 1000 cm^{-1} is observed start from early stage of NH_3 removal and achieves 60 cm^{-1} in hydrogen chabazite. The frequency of this mode is known to be proportional to the fraction of Si-O bonds (Si/Al ratio) in the zeolite framework (Pichat et al., 1975). Thus we may suppose that the Si/Al ratio in the chabazite framework increases during calcination of its NH_4 -form, in agreement with our X-ray diffraction data. The dealumination of the framework may result, analogously to observations in other zeolites, from partial hydrolysis of the framework aluminum by residual water and protons formed after removal of ammonia (Weeks et al., 1975; Shannon et al., 1985). If so, the amount of catalytically active hydroxyl groups produced at deammoniation is likely to be less than that expected from an "ideal" structure of hydrogen chabazite.

Further high-resolution ^{27}Al NMR study will permit to analyze the extent of dealumination and the nature of non-framework Al species formed at calcination of NH_4 -chabazite.

Beyer HK, et al, *J. C. S. Faraday T 1*, **73**, 1111-1118, (1977).

Passaglia E, *Proc. Chem. Soc.*, 45-52, (1975).

Pichat P, et al, *J. C. S. Faraday T 1*, **70**, 1402, (1975).

Weeks TJ, et al, *J. Catal.*, **38**, 461-468, (1975).

Shannon RD, et al, *J. Phys. Chem.*, **89**, 4778-4788, (1985).

HEAT CAPACITIES AND DERIVED THERMODYNAMIC PROPERTIES OF GLASSES AND LIQUIDS IN THE SYSTEM $Na_2O-B_2O_3-SiO_2$

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The wide range of applications of borosilicates, from laboratory glassware to nuclear waste disposal is well established. Yet, comparatively few studies have been done on the thermochemical properties of this system. However, these measurements are badly needed to determine entropies of melts, and especially to understand the relative importance of the contributions to the entropy stemming from thermal vibrations and temperature-induced structural changes. The heat capacities (C_p) of four sodium borosilicate glasses have been measured from 15 K to the temperature of the glass transition using an adiabatic calorimeter, a differential scanning calorimeter and an ice calorimeter using the drop method. Results shows that there exist deviations of C_p from an ideal-solution model with oxides as component in the system $Na_2O-B_2O_3-SiO_2$. This nonideality may be related to B-coordination differences between pure B_2O_3 , where boron is essentially three coordinated by oxygen atoms, and investigated glasses, where boron is distribute in various species (BO_4 , BO_{3A} , BO_{3S}); on the other hand, these deviations could be also associated with peculiar interactions between B and Si. Results allowed to determine the partial molar heat capacities of boron and sodium oxides in the silica-rich part of this system in the glass state. Drop calorimetry has been used to measure the C_p of the liquids in this system. At the glass transition, the C_p of liquids is from 18 to 30% higher than that of glasses. The C_p of sodium borosilicate liquids has a markedly non-linear composition dependence and shows negative temperature dependences. These anomalous variations could be associated with peculiar interactions between B and Si. Implications to the derived entropy and configurational properties will be discussed.

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PHASE RELATIONS OF HYDROUS MID-OCEAN RIDGE BASALT WITH IMPLICATIONS FOR LOWER MANTLE MINERALOGY

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Subduction of oceanic lithosphere into the deep Earth's interior is supposed to create chemical heterogeneity in the lower mantle. It was found recently, that anhydrous basalt have different melting temperature and density changes with depth relative to peridotite (Hirose et al., 1999). Study of water-bearing basalt might be also important for identification of possible hydrous phases in the basaltic composition, changes in phase transitions, and seismic anomalies. Phase relations in the hydrous MORB were determined at 18-25 GPa and temperature range between 1000 and 2400°C. There were no dense hydrous phases, which are stable in the MORB at 18-25 GPa. We observed the expansion of stability field of Al-rich perovskite and NAL-phase (Miura et al., 2000; Mijajima et al., 2001) to the lower pressures. Al-rich perovskite was observed below 1400°C at 25 GPa, whereas in anhydrous experiments it is stable above 27 GPa at 1400°C. NAL-phase occasionally stable at 20-25 GPa and temperature below 1200°C. At the higher temperature, NAL-phase is replacing by CAS-phase. We have supposed influence of water on stability field of the perovskite and provided additional experiments on water solubility in Al-rich perovskite in the Fe-bearing and Fe-free systems. FTIR data suggest that Al-perovskite can contain about 100-200 ppm H₂O. In the MORB composition, lawsonite and phengite are stable up to 12-13 GPa under slab conditions (Schmidt and Poli, 1998). At the higher pressure, distribution of water to the MORB components is very restricted. Trace amount of water can be stored in garnet, stishovite (Bolfan-Casanova et al., 2000), and perovskite. Therefore, MORB cannot be considered as important water carrier to the lower mantle. We ascertain that water in the MORB can evaluate local variations in the density anomalies at the top of the lower mantle.

Bolfan-Casanova N, Keppler H & Rubie DC, *Earth Planet. Sci. Lett.*, **182**, 209-221, (2000).

Miura H, Hamada Y, Suzuki Tet al, *Amer. Mineral.*, **85**, 1799-1803, (2000).

Mijajima N, Yagi T, Hirose Ket al, *Amer. Mineral.*, **86**, 740-746, (2001).

Schmidt MW & Poli S, *Earth Planet. Sci. Lett.*, **163**, 361-379, (1998).

Hirose K, Fei Y, Ma Y, Mao HK, *Nature*, **397**, 53-56, (1999).

DIAMOND GENESIS: EXPERIMENTAL SOLUTION

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Disclosing the chemical conditions of diamond formation in the Earth's mantle is the key to solution of the problem of diamond genesis. Based on mineralogical evidence, it is suggested that the primary fluid (Schrauder & Navon, 1994) or sulphide (Bulanova, 1995) inclusions in diamonds from

kimberlite deposits may be alternatively considered as parental growth media. Successful experimental programs on diamond syntheses in multicomponent carbonate - silicate - carbon (Litvin & Zharikov, 2000) and sulphide - carbon (Litvin et al., 2002) systems properly accounting for the natural fluid and sulphide prototypes are realized.

Diamond synthesis at 5.5 - 8.5 GPa in carbonate - silicate ("fluid") and sulphide melts oversaturated with dissolved carbon is the direct evidence of the high efficiency of both the natural parental media for diamond formation. The experimental carbonate - silicate melts similar to the natural ones belong to the multicomponent system K₂O - Na₂O - CaO - MgO - FeO - Al₂O₃ - TiO₂ - P₂O₅ - SiO₂ - Cl - CO₂ - H₂O - C. The experimental sulphide - carbon melts much like to the natural ones belong to the system Cu - Fe - Ni - S - C. In either case, physicochemical mechanism of diamond formation is conceptually identical and controlled by PTN - diagram of carbon oversaturation for the relevant system (N = dissolved carbon concentration in melt). Diamond formation in the carbonate - silicate (carbonatite) and sulphide solvents is characterized by multitude spontaneous nucleation. Numerous octahedron - shaped crystals, spinel - law twins, and oriented crystalline aggregates are formed. Crystal morphological and physical properties of the carbonatite - synthetic and sulphide - synthetic diamonds show their similarity to natural diamonds.

Thus, existence of two types of natural diamond - producing media in the Earth's mantle conditions is experimentally established and agrees with mineralogical data for syngenetic inclusions in natural diamonds. It seems reasonable to say that the bulk of natural diamonds was crystallized rather in silicate - rich carbonatite melts with dissolved carbon than in sulphide ones. Nevertheless, the true chemistry of the parental media for natural diamonds can result from specialized mineralogical tests.

Schrauder M & Navon O, *Geochim. Cosmochim. Acta*, **58**, (1994).

Bulanova GP, *J. Geochem. Explor.*, **53**, (1995).

Litvin YA & Zharikov VA, *Doklady Earth Sciences*, **373**, (2000).

Litvin YA, Butvina VG, Bobrov AV & Zharikov VA, *Doklady Earth Sciences*, **382**, (2002).

Cr₂O₃: THE UNFORGETTABLE BUT FORGOTTEN OXIDE IN MANTLE PARTIAL MELTING PROCESS

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Chromium is a highly compatible element and its importance to melting phase relations may not be obvious from the study of the melts themselves. Therefore, direct partial melting experiments are highly desirable. No any systematic work, however, has been done and chromium has been forgotten.

To investigate the chromium effect on mantle partial melting, piston-cylinder experiments have been carried out at 11 kbar in the model mantle system CMAS-Cr₂O₃. Previous experiments using traditional experimental technique were not successful due to some special chemical behaviours of this model mantle system: 1) Chromium has variable valance states and oxygen fugacity is critical to the experiments; 2) Partial melting along the solidus in the spinel peridotite stability field is isobarically

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pseudo-invariant; 3) Melt composition becomes increasingly picritic and quench crystallisation more serious with increasing Cr/(Cr+Al) ratio.

In order to circumvent these problems, we used some new experimental techniques and took new experimental rationale to carry on the study. Recent experiments are successful and suggest that: 1) Chromium dramatically changes the compositions of the pyroxenes, the major contributors to the mantle melting process. 2) Chromium raises the solidus of system CMASCr. The solidus increases are not linear with the Cr/(Cr+Al) ratio in the bulk compositions but are very strong at low Cr/(Cr+Al) ratios, very weak at median Cr/(Cr+Al) ratios and very strong again at high Cr/(Cr+Al) ratios. 3) Partial melting reaction in system CMASCr is totally different and spinel joins forsterite to be in a reaction relation with melt. 4) A wide range of melt composition is observed. As the Cr/(Cr+Al) ratio in the bulk composition increases, melt becomes less An-normative but more En-normative

ACCURATE DETERMINATION OF THE SOLIDUS OF SIMPLIFIED SPINEL LHERZOLITE IN THE SYSTEM $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (CMAS) AT 11 KBAR: TRADITIONAL AND NEW EXPERIMENTAL TECHNIQUES

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The solidus of simplified spinel lherzolite in system CMAS at 11 kbar were determined by traditional forward partial melting experiments (TE), sandwiched K_2O -doping forward partial melting experiments (SKE) and reversal experiments (RE). All experiments indicate the solidus is 1320°C, 30 degrees lower than the literature data (Presnall et al., 1979).

The TE bracketed the solidus between 1300°C and 1310°C. Considering the water influence, we believe the solidus would be higher.

The SKE took new experimental techniques. In these experiments, a glass layer of melt composition was put between two layers of crystalline mixture. The composition of the glass came from Walter & Presnall (1994) and 1%, 3% or 10% K_2O was added in. In system CMAS, melt coexists with Fo+Sp+Opx+Cpx only at one single temperature at any specific pressure. The introduction of K_2O split the temperature point into a temperature interval and the assemblage of Fo+Sp+Opx+Cpx+Melt was achieved. In order to overcome the water problem, outside buffer Fe_2O_3 was exploited. The K_2O content of the melts in those experiments displaying Fo+Sp+Opx+Cpx+Melt was extrapolated back to 0 K_2O and the solidus, 1319°C, was reached. Following the same principle, the glass composition at the solidus was derived from the collected phase composition data of those experiments.

The RE demonstrated that the melt composition derived from the SKE is indeed multiply saturated by Fo, Sp, Opx and Cpx and the solidus is around 1320°C.

The data collected in the SKE are combined with some literature data to generate an empirical geothermometer.

Presnall et al, 1979, *J. Petrol.* 20, 3-36

Walter & Presnall, 1994, *J. Petrol.* 35, 329-359

THERMODYNAMICS AND CRYSTAL CHEMISTRY OF Al SUBSTITUTED HEMATITE AND GOETHITE

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Synthetic samples of goethite-diaspore (FeOOH-AlOOH) and hematite-corundum ($\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$) solid solutions were investigated using high-temperature oxide-melt calorimetry and Rietveld refinement of X-ray diffraction powder patterns. The mixing enthalpies are positive (~10 kJ/mol at $X_{\text{Al}} = 0.2$) and of comparable magnitude, when normalized per one cation. The equilibrium solubility of corundum in hematite and diaspore in goethite at 298 K is negligible. The enthalpies of mixing in the hematite-corundum solid solution series show no temperature dependence between 298 and 1000 K. The excess enthalpies of mixing are too large to reproduce the experimental phase diagram (Muan and Gee 1956), unless excess entropies in the solid solution are considered. The thermodynamics of variable ordering schemes of composition FeAlO_3 was explored by static lattice energy calculations, using program GULP (Gale 1997). The calculations, in qualitative agreement with the calorimetric results, show that the disordered (corundum-like) configuration is highest in energy. Ordered (ilmenite- and LiNbO_3 -like) configurations are somewhat more stable in terms of energy but they lack the configurational entropy, and therefore are not observed in the system. The excess volume of mixing is positive for Al-hematite but almost ideal for Fe-corundum. Moreover, the degree of deviation from Vegard's law for Al-hematite depends on the thermal history of the samples. Introduction of Al into the hematite structure causes varying distortion of the hexagonal network of oxygen ions while the position of the metal ions remains intact. Distortion of the hexagonal network of oxygen ions attains a minimum at a composition $\text{Fe}_{0.95}\text{Al}_{0.05}\text{O}_3$. The excess volume of mixing in the goethite-diaspore solid solution is positive. The observed degree of Al substitution in natural goethite and hematite is probably controlled by nucleation pathways and slow kinetics of transformation to the stable phase assemblage rather than thermodynamic properties of the solid solutions.

Gale JD, *J Chem Soc, Faraday Trans*, 93, 629-637, (1997).

Muan A & Gee CL, *J Am Ceram Soc*, 39, 207-214, (1956).

ZIRCONOLITE: EXPERIMENTS ON THE STABILITY IN HYDROTHERMAL FLUIDS

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As a principal host for actinides and certain fission products (e.g., REEs (rare earth elements)), zirconolite is a major constituent of Synroc. Hydrothermal experiments were carried out with various fluids over a range of temperatures at 50 MPa to study the corrosion behavior of zirconolite. Experiments were performed in a closed system with single-phase, polycrystalline zirconolite-2 M, doped with REEs, Hf and U as actinide analogues and/or neutron absorbers.