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### ANALYSIS OF ISOTOPICALLY DOPED REACTION RIMS: A MULTILAYER MOVING BOUNDARY DIFFUSION MODEL

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Milke et al. (2001) produced polycrystalline enstatite reaction rims between forsterite with normal isotope compositions and quartz extremely enriched in <sup>18</sup>O and <sup>29</sup>Si at 1000°C and 1 GPa. Enstatite grew from the original quartz-forsterite interface into both directions. The <sup>29</sup>Si/<sup>28</sup>Si-<sup>29</sup>Si profile is symmetric across the reaction rim. The <sup>18</sup>O/<sup>16</sup>O+<sup>18</sup>O profile is skewed with a shallow gradient in the compartment of the rim which replaced quartz and a steep gradient in the other compartment. Milke et al. (2001) used the formalism of Le Claire (1963) to extract grain boundary diffusion data. This formalism was designed for systems with fixed geometry. This is a severe limitation in the context of rim growth. We suggest a model, where quartz, forsterite and the two compartments of the enstatite rim are treated as distinct media. The rim thickness increases with time, and the geometric effects of forsterite and quartz consumption are taken into account. The four media are coupled through the conditions of mass conservation and isotopic equilibrium between coexisting phases. Oxygen and silicon bulk diffusivities in the enstatite reaction rim derived from our model are:  $D_{Si,En}^{bulk} = 3.4 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$  and  $D_{O,En}^{bulk} = 4.1 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$  in the compartment of the reaction rim which replaced forsterite and  $1.9 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$  and  $3.7 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$  in the compartment, which replaced quartz. The silicon diffusivities obtained are approximately equal in the two compartments of the reaction rim. Using  $D^{gb} = D^{bulk} * \delta / d$ , where  $d$  is grain size (2  $\mu\text{m}$ ) this translates to  $D_{Si,En}^{gb} * \delta = 2 \times 10^{-22} \text{ m}^3 \text{ s}^{-1}$ , about two orders of magnitude faster than derived from LeClairs formalism. Oxygen diffusivity was by about one order of magnitude larger in the compartment of the reaction rim which replaced quartz than in the other compartment. The reason for this behavior and for the lack of the same effect in the silicon system is still unclear.

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### THE INFLUENCE OF PRESSURE AND WATER ON TRACE ELEMENT PARTITIONING BETWEEN CLINOPYROXENE, AMPHIBOLE AND BASANITIC MELTS

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Clinopyroxenes and amphiboles crystallized from a basanite by Adam & Green (1994) and Fujinawa & Green (1997) were re-analysed by LAM ICP-MS for Li, Rb, Be, Sr, Ba, B, Ga, Y, Zr, Hf, Nb, Ta, La, Ce, Sm, Ho, Yb, Lu, Th and U. The results confirm earlier observations of a negative correlation between

D values for REE and HFSE and pressure at near constant temperature (1000-1050 °C). Estimated values of  $R_0$  and E for REE are near constant with  $R_0 = 1.030\text{-}1.045 \text{ \AA}$  and  $E = 285\text{-}316 \text{ GPa}$  for both clinopyroxene and amphibole at 0.5 to 2.0 GPa. There is an approximately linear correlation between  $\ln D_0$  for cations in  $M2^{cpx}$  and  $M4^{amph}$  sites and  $e^2$  (where  $e$  = formal valency of a particular cation minus the average valency of cations in the same site).  $D_0$  for REE and HFSE are also positively correlated with both  $Al^{iv}$  in T sites and average cation valencies in  $M2^{cpx}$  and  $M4^{amph}$  sites, consistent with an electrostatic control of  $D_0$  inside individual crystallographic sites. However, the changes in  $Al^{iv}$  and average valency are quite small and seem insufficient to explain the magnitude of the changes in  $D_{REE}$  and  $D_{HFSE}$ . If our data are linked to the findings of Wood & Blundy (1997) it can also be argued that the negative correlations between  $D_{REE}$  and  $D_{HFSE}$  and pressure are due (at least in part) to increased concentrations of  $H_2O$  at higher pressures. By decreasing the  $\Delta G$  of fusion of REE and HFSE components in amphiboles and clinopyroxenes,  $H_2O$  reduces  $D_0$  values, thereby producing a negative correlation between partition coefficients and  $H_2O$  at constant temperature.

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### HIGH-PRESSURE PHASE EQUILIBRIA AMONG GARNET, ILMENITE AND PEROVSKITE IN THE SYSTEM $MgSiO_3$ - $Mg_3Al_2Si_3O_{12}$ : PHASE TRANSITION EXPERIMENTS AND CALORIMETRY WITH APPLICATION TO MINERALOGY OF THE MANTLE

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Phase equilibria in the system  $MgSiO_3$ - $Mg_3Al_2Si_3O_{12}$  were examined by high pressure experiments and also by calorimetry and thermodynamic calculation in order to investigate phase transitions of majorite garnet in the mantle of relatively low temperature regime such as subducting slabs. The phase transition experiments up to 27 GPa at 1000°C by a multi-anvil apparatus showed that majorite garnet transforms to ilmenite solid solution and subsequently to perovskite solid solution and that ilmenite solid solution is stable in the whole compositional range. Ilmenite of pyrope composition is stable below about 1200°C at about 25-27 GPa. These results are quite different from phase relations at 1600°C in which garnet transforms directly to perovskite and ilmenite solid solution is stable only in composition very close to  $MgSiO_3$ . Calorimetric measurements of enthalpies of ilmenite solid solutions showed an almost linear relationship with composition. Using the measured transition enthalpies, the phase relations in the system were calculated. The calculated phase boundaries confirmed that the stability field of ilmenite solid solution expands rapidly to pyrope-rich composition with decreasing temperature. The above results are applied to phase transitions of majorite garnet in the mantle. Assuming that mantle composition is pyrolite and its geotherm is lower by 600°C than that in average mantle, majorite garnet first transforms to ilmenite

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at depth range of about 620-680 km and further to perovskite at about 710-750 km. The post-spinel transition occurs at about 680 km between the two broad transitions. Calculation of density and seismic velocities based on the phase relations shows that, in subducting slabs near the top of the lower mantle, steep gradients of density and velocities can be observed above and below the sharp discontinuity at 680 km.

#### CHARACTERIZATION OF AN OH-RICH TOPAZ OCCURRING IN A KYANITE QUARTZITE FROM SULU UHP TERRANE, EASTERN CHINA

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Pure hydroxyl topaz,  $\text{Al}_2\text{SiO}_4(\text{OH})_2$ , has been synthesized at very high-pressure (Wunder et al., 1993), but usual natural compositions range from pure fluor topaz in rhyolites, to about  $\text{Al}_2\text{SiO}_4\text{F}_{1.4}(\text{OH})_{0.6}$  in hydrothermal deposits (Barton et al., 1982). The OH-richest topaz with  $X_{\text{OH}} = \text{OH}/(\text{OH}+\text{F}) = 0.41$  has been recently reported from a kyanite quartzite from the Sulu UHP terrane in Hushan, Donghai area (Zhang & Liou, 1999). An OH-rich topaz has been collected in the same locality (Ferrando et al., 2002). It shows: good {001} cleavage, weak birefringence, mean refraction index of 1.63 and the lowest  $2V\gamma$  value  $33(2)^\circ$  ever reported for natural topaz, close to  $28(2)^\circ$  determined for pure hydroxyl topaz (Wunder et al., 1993).

X-ray  $\text{MoK}\alpha$  single-crystal diffraction data were collected and the crystal structure was refined in the space group  $Pbnm$  to  $R = 0.023$ . The refined electron content of the F/OH site shows a random substitution between the two ions and  $X_{\text{OH}} \sim 0.5$ . The refined cell parameters are:  $a = 0.4669(8)$  nm,  $b = 0.8849(2)$  nm,  $c = 0.8392(2)$  nm. By using the determinative curves of Ribbe (1982), the measured values of both the edge  $b$  and the volume  $V$  give  $X_{\text{OH}} = 0.31$ . This mean value satisfactorily agrees with the average F content analyzed by WDS electron microprobe. The chemical analyses show zoning in the F content, with  $X_{\text{OH}}$  in the range between 0.21 and 0.39.

The fitting of the  $2V\gamma$  value to the relevant determinative curve of Ribbe (1982) gives  $X_{\text{OH}} = 0.45$  which is significantly higher than the value expected from the chemical analyses. Although this disagreement could be due to the combined effect of chemical zoning and difficulties in  $2V\gamma$  measurement, it could also be interpreted as the effect of different growing P/T conditions, i.e. HP/UHP vs. low-pressure metamorphic condition.

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#### SPECTROSCOPIC CHARACTERIZATION OF AN HERCYNITE-BASED PIGMENT

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Two samples of an hercynite-bearing pigment, with and without titanium, were investigated by means of mineralo-chemical techniques (XRD, EMPA, AAS), together with advanced spectroscopies (Mössbauer, EPR) and magnetic measurements (SQUID susceptometer), in order to characterize the overall electronic properties of the bulk material. The two samples are mainly constituted by corundum and contain up to 3.5 wt% hercynite ( $\text{FeAl}_2\text{O}_4$ ). The pigment with Ti shows a strong blue color, whereas the other one shows a pale sky-blue hue. In the Ti-bearing pigment small amounts of Ti are revealed from EMPA analysis of hercynite grains. The Ti valence state has been established as tetravalent on basis of EPR results, which excluded the presence of  $\text{Ti}^{3+}$ . Mössbauer data point to  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios corresponding to 90/10 and 87/13 in the Ti-bearing and Ti-free samples, respectively.  $\text{Fe}^{2+}$  is mainly distributed in tetrahedral coordination (T site of hercynite) and  $\text{Fe}^{3+}$  in the octahedral one (M site of hercynite and/or corundum). The complex EPR spectra of the two samples may be attributed to two different species of  $\text{Fe}^{3+}$ , the first of which presents features practically unchanged in the two samples. The EPR line of this species is due to a distorted Me-vacancies complex, with a very high zero-field splitting anisotropy. The other signal, very narrow and symmetrical, attributed to  $\text{Fe}^{3+}$  in a regular polyhedron coordination, is strongly related to the presence of Ti in the sample. As concerns magnetic investigations, deviations from the expected Curie-Weiss behaviour were detected at temperatures lower than 50 K, thus suggesting the presence of antiferromagnetic interactions. On the basis of the distribution and the interaction between Fe and Ti, revealed by all magnetic and spectroscopic investigations, a charge-transfer mechanism between  $\text{Fe}^{2+}$  and  $\text{Ti}^{4+}$  in hercynite may be invoked, which would account for the coloring properties of this pigment.

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### THE MISCIBILITY OF MELTS IN THE SILICATE-CARBONATE SYSTEMS

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There are many experimental data, which show the immiscibility of silicate and carbonate melts. These data are in contradiction with the structural compatibility of solid silicates and carbonates. They are able to form silicate-carbonate compounds and solid solutions. This is a reason to revise the results of these experiments. The wide miscibility gap was established by Koster Van Groos and P. Willie in the system  $\text{NaAlSi}_3\text{O}_8 - \text{Na}_2\text{CO}_3 - \text{H}_2\text{O}$ . We used the special technics, which allows to divide silicate and carbonate melts in the cardge. Our experiments showed, that there was no immiscibility in the system  $\text{NaAlSi}_3\text{O}_8 - \text{Na}_2\text{CO}_3 - \text{H}_2\text{O}$ . We also revised the experimental data of Freeston and Hamilton (1980), Brooker (1998) etc on the immiscibility of felsitic, nefelinitic, phonolitic melts and carbonate ones. There is an uncorrect graphic interpretation of the experimental data in these papers, because compositions of the melts are shown on the triangle diagram, which has no carbonate top. We recalculated these data and put them on the triangle diagram with tops:  $(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2) - \Sigma \text{Me}_x\text{O} - \Sigma \text{Me}_x\text{CO}_3$  and showed that the main part of the carbonate melts represented by carbonate component only and does not contain silicate components. It is obviously that this situation will be able if the carbonates are crystallised from homogeneous melt and is not the liquid, which appears as a result of immiscibility. The cause of mistakes of the experimental data in the silicate-carbonate systems is the confined possibility of the quenching method, when carbonate melt is unable to transform to glass. The project is supported by RFFR, grant 99-05-65408

### COMPRESSION MECHANISMS OF COESITE

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Understanding the thermodynamics of coesite has become increasingly important as it is discovered in more UHP terraines. However, the elastic properties of coesite are very anomalous (Angel et al., 2001). We have now undertaken a single-crystal X-ray diffraction study of coesite to pressures in excess of 8 GPa in order to determine the underlying structural reasons for this behaviour.

The structure of coesite is a three-dimensional framework of corner-linked  $\text{SiO}_4$  tetrahedra similar to that of feldspar (Megaw, 1970). But it is unusual in that it contains a straight Si-O-Si linkage that is the only bridge between two parallel semi-close-packed planes of oxygens. The distance between the two oxygen planes does not change with pressure, although the Si1-O1 distances forming the bridge shorten by 2%, indicating that mutual repulsion of the planes keeps the Si-O1-Si link in tension and thus linear. The major change upon compression involves the rotation of the Si2 tetrahedra about

[001], which increases the torsion angle between two adjacent Si2 tetrahedra along the *c*-axis and closes the "crankshaft" chains of tetrahedra by a shearing motion. These are the structural reasons for the anomalous positive value of one of the off-diagonal components of the elastic compliance tensor,  $s_{23}$ , of coesite and thus the initial softening of the *c*-axis under compression (Angel et al., 2001). The eventual stiffening of the structure, and the anomalous positive value for the second derivative of the bulk modulus of coesite, has no obvious structural cause that we can detect. But it may be related to the rotation mechanism being constrained by repulsion between the two semi-close-packed oxygen layers.

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### MODEL INDEPENDENT PHASE EQUILIBRIUM CONSTRAINTS ON FERROSILITE ACTIVITY IN THE BINARY Fe-Mg ORTHOPYROXENE SOLID SOLUTION

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Reversals of orthopyroxene (Opx) composition on the enstatite (En,  $\text{Mg}_2\text{Si}_2\text{O}_6$ )-ferrosilite (Fs,  $\text{Fe}_2\text{Si}_2\text{O}_6$ ) join equilibrated with hematite (Hm), magnetite (Mt) and quartz (Qz) were obtained in piston-cylinder apparatus in the pressure range 10-25 kbar at temperature 800 and 950°C. Double capsule technique with the Hm-Mt external buffer was employed to ensure the presence of both iron oxides in the run products. Starting materials were crystalline mixtures of synthetic Opx with  $X(\text{Fs}) (= \text{Fe}/(\text{Fe}+\text{Mg})) = 0.05$  and 0.45, synthetic Mt, reagent Hm and natural Qz finely ground together in stoichiometric proportion. Run products were carefully examined using optics, SEM, BSE imaging and wavelength dispersive electron microprobe. Despite the differences in the rates of forward and backward reactions  $\text{Fs (in Opx)} + 2\text{Hm} = 2\text{Mt} + 2\text{Qz}$  (1), very tight compositional brackets (less than 0.01  $X(\text{Fs})$ ) were obtained at each P-T. At 800°C midpoints of the compositional brackets are: 0.195/10 kbar, 0.24/15, 0.29/20 and 0.34/25; at 950°C: 0.21/15 kbar, 0.25/20 and 0.295/25 kbar. Activities of Fs, recalculated from these compositions using either Berman and Aranovich (1996) or Holland and Powell (1998) data sets for the pure end-member reaction (1), show negative deviation from ideal mixing. Strongly temperature dependent enthalpy of mixing is required to make these activity values consistent with the configuration entropy of the solid solution deduced from the site occupancy measurements. Simple mixture model with temperature dependent W term, similar to that of Berman and Aranovich (1996), adequately reproduces experimental data.

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### THE COMPOSITIONAL EVOLUTION OF DIFFERENTIATED LIQUIDS FROM THE SKAERGAARD LAYERED SERIES AS DETERMINED BY PHASE EQUILIBRIA MODELING

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Based on the COMAGMAT-3.65 crystallization model a set of phase equilibria calculations at  $P=1$  kbar and closed-to-oxygen conditions has been conducted for 65 rocks representing the principle units of the Layered Series of the Skaergaard intrusion. It allowed us to define the range of initial temperatures (1145 to 1085°C) and oxygen fugacities (1-1.5 log units above  $QFM$  to slightly below  $QFM$ ) intrinsic to the original crystal mush from which the rocks from LZa to UZa have been crystallized. In parallel, average major-element compositions of residual (interstitial) liquid were calculated demonstrating a trend of continual enrichment of  $FeO^*$  (up to 18 wt.%) and  $TiO_2$  (up to 5.5 wt.%) with only minor variations in the  $SiO_2$  contents (48 to 50 wt.%). Projection of the compositions onto  $OLIV-CPX-QTZ$  diagram evidences for the most of the Layered Series was crystallized on  $Ol-Pl-Cpx$  cotectic along with oxides. Estimated amounts of interstitial melts trapped in the Skaergaard "cumulates" range around 50 wt.%. Wager's compositions inferred from simple mass-balance were found to lie too far from the  $Ol-Pl-Cpx$  boundary to represent a realistic approximation of the low-pressure Skaergaard magma evolution. The main problem of genetic interpretations of the Skaergaard intrusion is shown to be a strong misbalance (Si, Ti, P) between the parental compositions followed from marginal rocks and the results of phase equilibria calculations and that of the whole differentiated body. One possible explanation is to assume the Skaergaard magma came to the chamber with an amount of crystals ( $Ol+Pl$ ) equilibrated with the calculated parental liquid. However, even if some amount of "hidden" troctolitic material exists, it is problematically that crystallization in a closed system could produce large volumes of rocks so rich in Fe-Ti oxides without complementary more felsic differentiates.

### AN EXPERIMENTAL CALIBRATION OF THE BIOTITE GARNET FELDSPAR QUARTZ GEOBAROMETER

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The biotite-garnet-feldspar-quartz assemblage involves different partial equilibria among which:

- (1)  $2Phl+3An+3Qtz=3Prp+Grs+2Kfs+2H_2O$
- (2)  $2Ann+3An+3Qtz=3Alm+Grs+2Kfs+2H_2O$
- (3)  $Phl+Alm=Ann+Prp$
- (4)  $3Ann+6An=3Sd+6aQz+2Gr+Alm$
- (5)  $3Eas+12An+6Ann=4Gr+2Py+12aQz+9Sd$

The geobarometric properties of equilibria (1) and (2) have been tested using a series of experiments carried out to understand the melting behaviour of metagreywackes (Vielzeuf and Montel, 1994). Thirty experiments in the range 5 to 24 kbar and 800 to 950°C show the coexistence of biotite, garnet, plagi-

clase and quartz. Consistent variations in phase proportions and compositions are observed as a function of pressure increase. In particular, the proportions of biotite and feldspar decrease while the garnet fraction increases. In garnet, the grossular content increases from 1,6% at 5 kbar to 21% at 20 kbar. These changes can be ascribed to the pressure-dependent equilibria (1) and (2). Mineral compositions and thermodynamic modelling using two different data sets (Berman, 1988; Holland and Powell, 1998) allow the calculation of P and T of equilibration. Calculated T, with the Bt-Grt thermometer, differ significantly from the experimental temperatures (errors higher than 75°C in half cases). Assuming a  $H_2O$  activity of  $0.7 \pm 0.2$ , we were also able to calculate pressures. Below 10 kbar, there is a good agreement between calculated and experimental pressures though P are always underestimated by about 1 to 2 kbar. This deviation increases progressively towards high pressures and reaches 5 kbar at P of 20 kbar. The origin of this deviation is not yet understood but cannot be ascribed to the uncertainty on the activity of  $H_2O$  in the fluid phase. Using different starting materials, an intercomparison with the GASP geobarometer is in progress. Nevertheless, these experiments demonstrate that equilibria (1) and (2), and more especially (2), can be used to determine pressures in metasedimentary rocks devoid of aluminum-silicate below 12 kbar.

### NUMERICAL EXPERIMENT ON GARNET CRYSTALLIZATION

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The experimental investigations focus mainly upon phase equilibria and mineral thermodynamics. Study of the mineral growth under metamorphic P-T conditions is restricted by numerous difficulties. Instead numerical modelling can help. We considered the growth of garnet which is quite usual metamorphic mineral and may give us information about metamorphic processes.

The aims of our studies were: (1) the reconstruction of mechanisms and duration of the mineral growth, and (2) the reveal of the prevalent mechanisms producing growth zoning in garnets. We constructed the mathematical models describing both isothermal and nonisothermal crystal growth in closed systems and at fluid flow. Because of lack of experimental data on component distribution between Fe-Mg garnet and aqueous fluid we were compelled to calculate these distribution coefficients.

The numerical experiment displays that:

1. Garnet growth should be preferably surface-limited. This conclusion is confirmed by the morphological features of natural garnets.
2. The time of the garnet growth does not exceed 0.1-0.5 Ma but may be much shorter, depending on fluid supersaturation. It means that mineral growth is close to isothermal. The main crystallization way is desupersaturation.

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3. The prevalent mechanism producing growth zoning is fractionation in the closed system (the Rayleigh fractionation). Nonmonotonic zoning can appear at fluid flow through metamorphic rock.

4. The fractionation can produce both normal and reversed zoning. The normal zoning arises at the growth from the neutral aqueous fluid whereas the crystallization from alkaline fluid should result in reversed zoning.

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### PHASE TRANSFORMATIONS IN $\text{CaCO}_3$ AND $\text{SiO}_2$ UP TO 2.5 GPa FROM ELECTRICAL IMPEDANCE MEASUREMENTS

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The phase transformation in calcite I-IV-V, calcite  $\Leftrightarrow$  aragonite and in  $\text{SiO}_2$  have been characterised by electrical impedance measurements at temperatures 500-1200°C and pressures 0.5 - 2.5 GPa in a piston cylinder apparatus. The bulk conductivity  $\sigma$  has been measured from Argand plots in the frequency range  $10^5 - 10^2$  Hz. The cell represents a coaxial cylindrical capacitor with a geometric factor c. 6 cm [1]. As a starting material the synthetic polycrystalline powder of  $\text{CaCO}_3$ , natural crystals of calcite (Spain) and of quartz Mont Rose (France) were used. The transformation temperature was identified from a bulk resistivity-temperature curves as a kink point of the activation energy. In a low temperature phase (calcite I), the activation energy  $E_a$  of  $\sigma \cdot T$  is c.  $1.05 \pm 0.05$  eV, and in high temperature phase (calcite V)  $E_a$  is c.  $0.75 \pm 0.05$  eV. The pressure dependence of  $T_c$  for the transformation in calcite V is positive for pressures up to 1 GPa  $dT_c/dP \sim +20^\circ/\text{GPa}$  and becomes negative for the pressures 1-2 GPa:  $-20^\circ/\text{GPa}$ . The transformation calcite I -IV is less evident from the present observations. The activation energy of electrical conductivity between I and V phases increases gradually to from 0.95 to 1.05-1.15 eV and then decreases to c. 0.75 eV. The gradual increase of  $E_a$  may correspond to a kinetic phenomena of retaining R-3c symmetry at temperatures above c. 850°C. However, the pressure dependence of the kink of the activation energy is also  $+20^\circ/\text{GPa}$ . The kinetics transformation of calcite in aragonite has been monitored by measuring a variation of the electrical resistance of calcite at  $10^3$  Hz with time in the stability field of aragonite. Products of the phase transformation have been analysed with a powder diffractometer. Variations of the electrical resistance with time correlate with the degree of phase transformation  $\xi(t)$ . The degree of transformation calcite to aragonite has been fitted to the expression:  $\xi(t) \sim [1 - \exp(-t/\tau)]$ , where  $\tau$  is a characteristic time of the phase transformation at a temperature T. For example,  $\tau$  of the transformation of calcite to aragonite at 2.5 GPa and 760°C is 7.5 h, at 1.5 GPa and 680°C is 8.8 h. The temperature of a-b-phase transition in quartz has been characterise at 0.5, 1, 1.5 and 2 GPa from the electrical impedance measurements of

polycrystalline samples. The difference in activation energies of  $\sigma \cdot T$  in  $\alpha$ - and  $\beta$ - quartz is rather small and increases with the pressure. For example at 0.5 GPa the activation energies  $E_a$  of  $\sigma \cdot T$  for a and b-phase are 1.04 and 1.26 eV, at 1 GPa 1.1 and 1.3 eV, at 1.5 GPa 1.18 and 1.41 eV, at 2 GPa 1.23 and 1.53 eV, respectively. The calculated activation volume  $\Delta V$  for  $\alpha$ - and  $\beta$ -phases is about the same 0.18 and 0.25  $\text{cm}^3/\text{mol}$ . The estimated phase transition temperature  $T_c$  from heating and cooling cycles are slightly different.  $dT_c/dP$  obtained in this study from heating and cooling cycles is smaller than has been reported from laser interferometry  $256^\circ/\text{GPa}$  [2] and close to the  $T_c$  and  $dT_c/dP$  data reported in [3].

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### GROWTH OF TOPAZ SINGLE CRYSTALS FROM SUPERCRITICAL AQUEOUS FLUIDS AND ITS CHARACTERIZATION

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Topaz often occurs in some kinds of pegmatites, greisens and hydrothermal veins. Until the last time large crystals of topaz haven't been received, but a spontaneously crystallization was realized many times [1, 2]. However, topaz synthesis becomes an important problem because solving can help to comprehend the genesis of topaz in nature, and help to solve problem of synthesis of gem-quality crystals. Our team accomplished synthesis of topaz single-crystals, based on recently got experimental data on studying of processes of joint transfer of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in supercritical fluids in terms of straight temperature gradient [3]. Crystals were grown in autoclaves (volume 50  $\text{cm}^3$ ) with temperatures from 600 up to 800°C, pressures from 20 up to 200 MPa and temperature difference between top and bottom parts of autoclave from 20 up to 100°C. Acid (pH 1-2 after experiments) aqueous-fluorine fluid was chose as a crystallizing medium. Nutrient was presented by quartz and topaz single-crystal bars with ZX-orientation, sizes 4x4x50 mm, and was placed in the top part (colder part) of autoclave, and sections of topaz with different orientations were hanged up in the bottom part (the hotter part) of autoclave. Intense dissolution of nutrient bars and growth of topaz crystals were observed with fluid density from 0,1 to 0,45  $\text{g}/\text{cm}^3$  (pressure about 40-200 MPa). However with density less than 0,33  $\text{g}/\text{cm}^3$  quartz began intense transferring to the bottom part of autoclave and crystallizing there jointly with topaz as a small spontaneous crystals. In general, as a result of made experiments, a method of reproducible synthesis of topaz single crystals on seed (cuts {001} and {112}) with growth rates 0,15-0,22 mm/day is found.

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