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NANOTEXTURES OF LASER-HEATED BIOTITES

Cecilia Viti (vitic@unisi.it)¹, Marcello Mellini (mellini@unisi.it) & Gianfranco Di Vincenzo (g.divincenzo@iggi.pi.cnr.it)²

¹ Dip. Scienze della Terra Università di Siena, Via Laterina 8, 53100 Siena, Italia

² Istituto di Geocronologia e Geochimica Isotopica CNR, Via Moruzzi 1, 56124 Pisa, Italia

Chloritized biotites have been laser-heated according to four heating steps (laser power of 0.3, 0.7, 1.2, 2.2 W, corresponding to approximately 600, 810, 940, 1080°C, respectively; 2 min/step followed by 3 min of pumping out). Samples heated up to 600, 810, 940 and 1080°C have been investigated by high resolution TEM, in order to understand the structural and chemical transformation of biotite and interlayered chlorite. Most important results are: a) 600°C: biotite crystallinity is lower than in the untreated sample, reasonably due to dehydration processes. Chlorite breakdown is almost completed. b) 810°C: occurrence of diffuse delamination, 10-100 nm thick. Chlorite breakdown products start to crystallize. Main phases are spinels with variable composition, olivines and amorphous silica, occurring as irregular domains 10-20 nm in size, within the poorly crystalline biotite. c) 940°C: delamination is still present but it is reduced. Biotite is more crystalline than in previous sample. The chlorite breakdown products (olivines and spinels) form larger crystalline grains, typically elongated parallel to biotite (001). d) 1080°C: biotite (reasonably, oxybiotite) is characterized by higher crystallinity with respect to both treated and untreated samples, due to advanced structural annealing. EDS analyses performed on pure biotite domains are completely similar to those of the untreated biotite, thus indicating that biotite thermal transformation (i.e., dehydration followed by annealing at high temperature) was essentially isochemical. Olivine and spinels are hosted within perfectly euhedral negative crystals and show topotactic relation with the host biotite (thus, with the original chlorite): in particular [111]Spl parallel to [001]Bt(chl) and [100]Ol parallel to [001]Bt(chl). This evidence suggests that the crystallization of new phases is strongly influenced by the close packing of oxygens in the layer silicates; in particular the oxygen network of chlorite is inherited by its breakdown products.

STRUCTURE AND RHEOLOGY OF PERALUMINOUS MELTS: THE EFFECT OF Fe₂O₃

Sharon Webb (swebb@gwdg.de), H Büttner & E Müller

Geowissenschaftliches Zentrum Göttingen, Goldschmidtstr. 1, Göttingen, Germany

The Na₂O-Al₂O₃-SiO₂ system is used to model a large number of petrological processes. But even in this simple system there are anomalous changes in rheology as a function of composition. It has been previously shown for sodium-aluminosilicate melts that, at a constant temperature and constant SiO₂ content, there is a shallow maximum in viscosity in the vicinity of the subaluminous join. This maximum occurs within the peraluminous field, suggesting the presence of triclusters consisting of one aluminate and two silicate tetrahedra.

The viscosity of a range of Na₂O-Al₂O₃ compositions with 67 mol% SiO₂ and 0.60 > Na/(Na+Al) > 0.35, has been determined using the micro-penetration technique in the 8 < (log₁₀ Pa s) < 14 range. For these melts, at a temperature of 1050K, viscosity abruptly increases by 6.5 log₁₀ Pa s from an almost composition independent low viscosity for peralkaline compositions, to a composition independent viscosity as the melt composition becomes increasingly peraluminous. Thus, the shallow maximum in viscosity previously observed appears to be a plateau in viscosity for peraluminous composition Na₂O-Al₂O₃-SiO₂ melts. The activation energy for viscous flow also changes dramatically as a function of melt composition; increasing from ~480 kJ mol⁻¹ for the peralkaline compositions, to ~630 kJ mol⁻¹ for the peraluminous compositions. This suggests that the change in melt structure due to the change in Na:Al has a dramatic effect on the flow mechanism of the melt.

The substitution of Fe₂O₃ for up to 5% of the Al₂O₃ in this system results in a decrease in viscosity. The activation energy for viscous flow for the peraluminous composition melts is decreased by ~20% upon the substitution of Fe₂O₃ for Al₂O₃; but no change in activation energy is observed for the peralkaline compositions.

TEXTURAL DEVELOPMENT OF DEHYDRATION-MELTING IN AMPHIBOLITE AT 2.0 GPa AND 950°: EFFECT OF TIME

Zhou Wenge (wengzhou@sina.com)¹, Xie Hongsen¹ & Zhao Zhidan²

¹ Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, 550002, China

² Department of Geology, China university of Geosciences, Beijing 100083, China

We have carried out the dehydration-melting of a natural amphibolite (56vol.% hornblende, 44vol.% plagioclase), in multi-anvil apparatus, experiments at 2.0 GPa and 950° for 1-170 hours. The samples are put into graphite capsules, which are sealed in gold capsules. As the annealing time less than 4 hours, Liquid and garnet appeared in the boundary of plagioclase and hornblende, which indicates this reaction: Hb + Pl — Liquid + Gt. In the mean time, two other reactions took place: Hb — Cpx + H₂O and Pl — Ky + Na-Cpx + SiO₂. Melting dominated by the growth of clinopyroxene and garnet. Liquid interconnectivity is attained, as the annealing time is 7 hours, with only about 5% liquid. As the annealing time increasing (from 10 hours to 72hours), liquids increased rapidly along with the loss of plagioclase (Ky + Na-Cpx + SiO₂). As annealing time in range of 72-170 hours, only garnet and clinopyroxene is the solidus mineral. Most garnets are around the clinopyroxene. Garnet is enriched in pyrope. Liquids enrich first in An and then in Ab. And liquids are always silica rich (60-70 wt.% SiO₂), strongly peraluminous (2-5 wt.% normative corundum), very felsic (Mg + FeO* + TiO₂ less than 4wt.%). It is likely that segregation of initial liquids could not only effectively remove incompatible trace elements but although left the Gt + Cpx + Na-Cpx + Ky + SiO₂ assemble during the transition from amphibolites-faces to eclogite-faces.

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COORDINATION CHEMISTRY OF Fe IN HYDROUS SYNTHETIC GLASSES

Max Wilke (max@geo.uni-potsdam.de)¹,
Francois Farges², Harald Behrens³,
Stephanie Rossano², Valerie Malavergne²,
Laurent Gautron² & Pierre-Emmanuel Petit⁴

¹ Inst. f. Geowissenschaften, Universität Potsdam, 14415
Potsdam, Germany

² Laboratoire des Géomatériaux, Université de Marne la
Vallée, 77454 Marne la Vallée cedex 2, France

³ Inst. f. Mineralogie, Universität Hannover, 30167 Hannover,
Germany

⁴ ESRF, 38043 Grenoble, France

We present a combined, Mössbauer and high-resolution XANES spectroscopies at the Fe K-edge in synthetic glasses of the haplotonalitic ternary SiO_2 (Qz)- $\text{NaAlSi}_3\text{O}_8$ (Ab)- $\text{CaAl}_2\text{Si}_2\text{O}_8$ (An), containing 0.4-1.0 wt.% Fe. Similarly, a series of other Fe-bearing glasses was studied such as albite, orthoclase, anorthite, sodium trisilicate glass. High pressure, hydrated glass samples were quenched in an IHPV device from 200-500 MPa and 850-1000°C. The Fe^{3+}/Fe ratio of these glasses (between 0 and 0.6) was measured using ^{57}Fe - Mössbauer spectroscopy. Fe K-edge XANES spectra were collected at the ID26 beamline, using double-crystal Si(220) monochromator, ensuring a 1.1 eV core-hole lifetime convoluted by a 0.6 eV experimental resolution. A set of 25 model compounds containing Fe(II) and Fe(III) in 4 (T_d or D_{4h}), 5 (C_{3v}), 6 or 8-coordinated environments were collected in parallel to derive a coherent picture of the effect of redox state and coordination environment in the pre-edge and XANES spectra. To be independent from resolution effects, the pre-edge information was reduced to centroid position and integrated intensity. Glasses systematically show a doublet in the pre-edge spectra, their respective intensity increasing with increasing Fe^{3+}/Fe ratio. In parallel, the energy of the centroid increases with the Fe^{3+}/Fe in a non-linear fashion, suggesting that ferric and ferrous iron do not have the same coordination environments. The Fe^{3+}/Fe derived from pre-edge information is consistent with Mössbauer spectroscopy despite the pre-edge derived values are systematically shifted towards higher values as compared to those from Mössbauer spectroscopy. The pre-edge parameters obtained from the spectra of the glasses suggest mixture between 5-6-coordinated Fe(II) and mostly 4-coordinated Fe(III). There is a considerable effect of the network modifiers (Na, K, Ca) on the speciation of Fe(II) and Fe(III). The introduction of water in these glasses does not significantly affect the structure of the pre-edge spectra suggesting only negligible changes in the first coordination shell. However, major differences compared to the dry counterparts are observed in the XANES spectra at the main crest of the edge, which show dramatic signs of structural reorganizations around Fe as a function of quench rate. These changes are more significant for the tonalite and orthoclase glass than for the albitic one. Transmission Electron Microscopy (TEM) has evidenced a variety of nano-crystals which may be assigned to Fe-oxides in a tonalitic sample quenched at very low speed. Samples quenched more rapidly (> 150 K/min) do not show such nano-crystals. Our studies show that the extraction of redox information about Fe in glasses is not straightforward from pre-edge analysis if variations in speciation are not taken into account. Co-relation of the spectroscopic data with TEM imaging is done to elucidate the nature of the structural rearrangements responsible for the characteristics observed in spectra of the hydrous glass samples.

SIMULTANEOUS GROWTH AND DISSOLUTION PHENOMENA OBSERVED BY SPM ON HYDROTHERMALLY GROWN SPESSARTINE

Cornelis F. Woensdregt (woens@geo.uu.nl) &
Johannes D. Meeldijk

Faculty of Earth Sciences, Utrecht University, PO Box
80.021, 3508 TA Utrecht, The Netherlands

Spessartine ($\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) has been grown from hydrothermal solutions at temperatures ranging from 550°C (0.1 GPa) to 650°C (0.3 GPa). At the highest pressure and temperature {110} is dominant, while at intermediate temperatures and pressures corroded {100} determines the growth habit with {110}, {211} and {111} as minor forms.

Scanning Force Microscopy (SFM) shows the presence of growth spirals on {110}, {211} and {100} that are according to the Hartman-Perdok theory morphologically important F forms (Boutz and Woensdregt, 1993). On {110} the growth spirals have a rhombic shape due to the presence of two equivalent strong PBCs parallel to $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$. The form {211} is commonly striated and demonstrates macroscopically the typical features of an S (tepped) form. However, it is an F form, because of the presence of very elongated growth spirals.

Scanning Electron Microscopical (SEM) observations showed that the {100} are always dome shaped and often strongly corroded. These rough {100} interfaces are the dominant interfaces at the first stage of the crystallization at all temperatures and pressures. SEM observations demonstrate that, when the supersaturation decreases after 24 hours during the growth process at intermediate temperatures and pressures, flat {110} and {211} are becoming more stable and {100} is very strongly corroded. SFM observations show that an additional hopper-like layer spreads over the surface of {110} parallel to the edges between {110} and {100}. These hopper rims have steps with step height and a step width, which are much smaller than those of the original steps on {110}. They are formed due to the local supersaturation at the edge of the stable {110} caused by the dissolution of the unstable {100} interface.

Instead of the classical idea that habit changes are due to relative growth rate changes, we can now demonstrate habit change can also occur by simultaneous growth and dissolution.

Boutz MMR & Woensdregt CF, *J. Crystal Growth*, **134**, 325-336, (1993).

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DIRECT EXPERIMENTAL INVESTIGATIONS OF INITIAL MELT TEXTURES IN NATURAL, INTACT PELITIC AND GRANITIC ROCKS

Anke Wohlers (wohlers@mail.uni-mainz.de)¹,
Lukas Baumgartner
(lukas.baumgartner@img.unil.ch)² &
Christoph Hauzenberger (christoph.hauzenberger@kfunigraz.ac.at)³

¹ Institut fuer Geowissenschaften, Johannes Gutenberg-
Universitaet Mainz, 55099 Mainz, Germany

² Institute for Mineralogy and Petrology, University Lausanne,
1015 Lausanne, Switzerland

³ Institut fuer Mineralogie und Petrologie, Karl-Franzens-
Universitaet Graz, 8010 Graz, Austria

Migmatites occur at the western corner of the Little Cottonwood (LC) stock within the sill-kfsp zone. We have started a series of experiments to simulate the partial melting of these pelites. 25 Experiments were performed in cold seal vessels under H₂O-undersaturated and (near) H₂O-saturated conditions at 2 kb, at 700°, 750° and 800°C (167-508hrs run duration). Cores of 1 cm length and 0.3 cm diameter were drilled from andalusite-cordierite-biotite-muscovite-zone rocks of the LC contact aureole. The cores were loaded into 4 mm diameter gold capsules (with 60-125 ml of H₂O for water-saturated runs). Grain size of samples varied between 10 and 100 µm. After quench, melt and mineral compositions, as well as textures were analysed by SEM and electron microprobe.

Melt formed continuous seams along all grain boundaries. The initial texture, including grain shapes, are preserved. New minerals grew on specific textural sites, e.g. hercynite grew around the iron-titanium-oxides, and sillimanite and biotite nucleated in melt pools, which replaced muscovite. The amount of melt along grain boundaries depended on the run duration and amount of water added to the samples. Melt fraction is 48% for a sample run for 240 hrs at 800°C (water added), while a fraction of 53% was estimated for a run of 507 hrs at 800°C without additional water. A sample with the initial composition of qtz-ms-bt-crd-magnetite has a melt fraction of 24% after 186 hrs at 700°C and 58% after 330 hrs at 750°C. Melt on grain boundaries is compositionally zoned, with gradients of 1-2% in SiO₂, Al₂O₃, K₂O over a distance of 10 µm. Normative melt composition for a run at 800°C (with additional water) results is 88.5% quartz, 7.8% k-fsp and 3.7% albite. The water absent experiments yielded less normative quartz (82.7%), and more normative albite (7.4%).

STEPWISE ARGON EXTRACTION EXPERIMENTS AND CONVENTIONAL K-Ar DATA ON ILLITE-SMECTITE

Solomon Woldemichael (solomon@rins.ous.ac.jp),
Toshinori Okada & Tetsumaru Itaya

Stepwise argon extraction experiments and conventional K-Ar dating on 0.5-1.0 µm, 1-2 µm and 2-4 µm size fractions separated from hydrothermally altered late Miocene dacite provide information on argon releasing pattern and reliability of K-Ar dating of Illite-smectite (I/S). Up to 300 °C argon release patterns of I/S dominated by non-radiogenic argon, subsequently radiogenic argon quantity continuously increase and peak at about 500 to 700 °C. For 0.5-1.0 µm and 1-2 µm size fractions the radiogenic argon release reaches its maximum at

about 550-600 °C and insignificant amount argon was released at 1500 °C, whereas for 2-4 µm grain size fraction the radiogenic argon release reach its maximum at about 650-700 °C and significant amount of radiogenic argon released at 1500 °C. K-Ar ages of finer, 0.5-1.0 µm, fraction show tendency to be younger than coarse fractions from the same sample, also most of these age differences are within the error limits. All clay minerals in those rocks are hydrothermal minerals and primary minerals are plagioclase, K-feldspar, quartz, pyroxene and hornblende. Similar radiogenic argon releasing pattern for 0.5-1.0 and 1-2 µm fractions verify that little or no detrital K-feldspar phase present, whereas minor differences in argon release pattern for 2-4 µm grain size fraction suggest presence of small detrital K-feldspar. K-Ar ages of 0.5-1.0 m size fractions from seven samples range from 6.2 to 6.7 Ma. The K-Ar ages of 1-2 µm and 2-4 µm grain size fractions range from 6.7 to 7.0 Ma and 6.6 to 7.0 Ma respectively. These values are consistence with estimated age of the hydrothermal alteration, which is within 1 Ma of the age of host dacite (c 7.2 Ma).

INTERLAYER VACANCY CHARACTERIZATION OF SYNTHETIC DI- AND TRIOCTAHEDRAL (K,Rb,Cs,Ba)-MICAS BY IR-SPECTROSCOPY

Bernd Wunder (wunder@gfz-potsdam.de) &
Stefan Melzer

GFZ-Potsdam, Div. 4, Telegrafenberg, 14473 Potsdam,
Germany

Phlogopitic micas of the solid-solution binaries KMg₃[AlSi₃O₁₀](OH)₂ (phlogopite) - Rb-phlogopite, phlogopite - Cs-phlogopite, and phlogopite - BaMg₃[Al₂Si₂O₁₀](OH)₂ (kinoshitalite) were synthesized at temperatures of 700 and 800°C and pressures of 0.2 and 2.0 GPa. The run products were investigated by optical microscopy, X-ray powder diffraction, electron microprobe (EMP), and infrared (IR) spectroscopy. All runs yielded between 81 to 100 wt.% of phlogopitic micas, beside traces of quartz, sanidine, and in one run talc. Celsian and cymrite formed as additional phases in the runs of the (K-Ba)-series. Based on EMP-analyses, interlayer vacancy concentrations of up to 0.29 (p.f.u.) were determined, indicating a significant talc component within the synthesized phlogopitic micas. In addition to the known characteristic phlogopite OH-stretching vibrational bands, the IR-spectra of the synthetic trioctahedral micas with incompletely filled interlayer sites exhibit a further OH-band, centered in the spectral-range 3674 - 3678 cm⁻¹. The intensity of this band is correlated with the amount of vacancies. The vacancy concentration of phlogopitic micas was determined quantitatively from the intensity of this IR-band by using the intensity of the principal OH-band of synthetic talc as a standard. The vacancy concentration of the interlayer site determined by IR-spectroscopy agrees with the vacancy-values derived by EMP-analyses. Additionally, (K, Rb, Cs)-phengites were synthesized in the same PT-range. For these dioctahedral micas we determined interlayer vacancies concentrations of up to 0.27 by EMP-analyses. Such interlayer vacancies of phengitic micas can be chemically characterized by a pyrophyllite-component. However, no pyrophyllite-band was detected by IR-spectroscopy for the synthetic phengites. Therefore, our preliminary assumption is that the phengitic micas synthesized within this study do not exhibit any interlayer vacancies and that, in contradiction to the synthetic phlogopitic micas, the apparent EMP-determined vacancies only result from alkali-loss during the EMP-measurements.