XRF- AND EMP- INVESTIGATION OF GLASS COATINGS AND MELTED DOMAINS OF PEBBLES FROM CRATERS IN CHIEMGAU, GERMANY. V. Procházka[1] and T. Trojek[2], [1]Institute of Hydrogeology, Engineering Geology and Applied Geophysics, Charles University, Albertov 6, CZ-12843 Czech Republic (vprochaska@seznam.cz), [2]Czech Technical University, Nuclear and Phys. Engineering faculty, Břehová 78/7, CZ-11000 Praha 1 (tomas.trojek@fjfi.cvut.cz).

Introduction: Rock samples from two craters in the Chiemgau strewn field were investigated with methods selected for minimal destruction of this unique material, affected by short disequilibrium heating and extreme deformation most likely of impact origin [1,2]. Craters are developed in Quaternary terraces formed by pebbles of various rocks from Alps. Shock metamorphism including melting of the rocks has been well documented [1,2], however the questions about meteoritic contamination of the material collected still remain unanswered. Here we present a contribution to chemical characterization of various melt products in pebbles of silicate rocks.

Methods: Elements heavier than Mg were measured in flat surface of cut specimens, or in untreated glass surface, by Delta Premium XRF analyzer, using two beams with voltage 50 kV and 10 kV and spot diameter 1 cm (if necessary, beam diameter was reduced to 2 mm). For control, several measurements were also performed with a routine XRF analyzer consisting of Mini-X X-ray tube (35 kV, 10 μA) and SDD detector. The diameter of the analyzed area was approximately 3 mm. Another XRF device of proper construction [3] has been used for aerial element mapping with resolution 0.05 mm for thin glass coatings or highly porous "slags" in sections. The device consists of a molybdenum anode X-ray tube (XOS, Power Flux PF) with polycapillary focusing optics and an Si-PiN detector (Amptek, 6 mm^2 x 0.5 mm). The X-ray tube was operated at a maximum voltage of 50 kV and a maximum current of 1 mA, with acquisition time few seconds in each spot. In one sample the glass coating was also investigated by SEM and electron microprobe (TESCAN Vega with electron-dispersive analytical system and X-Max 50 detector).

Characterization of individual samples: Due to limited number of samples and full-value quantitative analyses for statistical evaluation, we prefer description of the most affected samples with simple comparison of chemical composition of the original rocks and of glass coatings or other melt products.

Locality Kaltenbach. Sample No. 123 – orthogneiss in places with limonitic crust, covered by green-colored glass of variable thickness except for the original bottom side (movement of melt on the pebble's surface is evidenced by higher glass thickness in dimples). Inside the rock consists of quartz, feldspars and green porous veinlets, probably dominated by melting products of biotite or chlorite (they have elevated content of Fe, K and Ti). The outer glass coating is enriched in Cu (up to 88 ppm).

Locality Emmerting (Krater 004): sample No. 407 – strongly melted granitic (or perhaps syenitic or monzonitic) rock, "welded" by a tongue of green glass (possibly eutectic melt) with calcareous sandstone (*Kieselkalk*), which is however macroscopically affected only in the 2 mm thick contact zone. Inside of the granitoid only feldspars and rare quartz are partly preserved as macroscopic mineral grains. The melt formed bluish and dark grey porous "slag", the dark one being enriched in Fe. Deformation of strongly melted domains can be observed, indicating high stress still before solidification. Moreover, colorless and brown glass occur on the surface (not analyzed). The eutectic (?) melt joining both pebbles is strongly enriched in Fe (9.7–11.3 %), also relatively enriched in Sr, Cu and Zn, and depleted in Si.

No. 409 – calcareous sandstone or impure limestone (*Kieselkalk*), with carbonate-poor reddish crust (slightly enriched in Cu and Zn) and thin white glass coating outside the weathering crust. The glass is strongly enriched in K, Cu (132–136 ppm), Zn, Rb and Sr.

No. 419 – highly porous re-melted (meta?)basic rock with prevalently thin greenish glass coating. The glass surface is systematically enriched in K (up to 7.5 % K_2O), Cu (up to 447 ppm), Rb, and Zn. Content of Ni remained below 25 ppm in all analyses and Fe was in the range 2.5–3.5 %.

No. 420 – orthogneiss with thin transparent glass coating, which is relatively enriched in K, Ca, Cu, Mn and Zn. According to EMP the glass has high content of alkalis with the sum (Na_2O+K_2O) = 9.0–13.6 %, peak Na_2O 9.0 % and peak K_2O 10.5 %. The composition suggests that the glass is derived from alkali feldspar, plagioclase and biotite (in few cases it is close to a transition between Na-, K- and Ca-feldspar). Newly formed phases in the glass include acicular diopside and plagioclase, and Fe-Mg(-Ti) oxides, which may form clusters of small euhedral crystals (magnesioferrite?), or symplectites with unidentified Al-rich phases. As a relict phase, only zircon was reliably identified in the glass; it shows some corrosion by the melt but not transformation to baddeleyite (which would require temperatures exceeding 1500 °C). At the boundary between orthogneiss and glass also extremely porous quartz occurs.

No. 421 – impure quartzite. Porous black veinlets are largely concordant with original foliation but also form some extrusions on the surface; they have elevated content of Fe (up to 6.2 %) and Mn (up to 0.32 %). Thin porous white veinlets also occur (not analyzed). The pebble is coated by thin greenish glass, slightly enriched in Cu (22–35 ppm), and irregularly by little porous brown glass, which is obviously youngest and penetrates discordantly through the pebble. The brown glass is slightly enriched in Fe (up to 5.5 %) and irregularly also rich in Ni (up to 82 ppm).

No. 422 – extremely deformed and partly melted gneiss with thin coating of glass rich in K and Cu (slightly elevated P and S could be related rather to an outer organic contamination).

Summary and discussion: Porous melt veinlets inside the pebbles were produced by disequilibrium shock melting (mainly of phyllosilicates, like biotite and chlorite), only locally significant eutectic melting followed. Their composition reflects the shock-melted minerals without detectable external contamination. The porosity is caused by escape of water vapor liberated from biotite and other H_2O-bearing minerals. Shock decomposition of Fe-bearing silicates may also have produced (sub-)microscopic oxide phases [4,5] which could be partly responsible for unusual magnetic properties of the rocks [2,6] (note that significant frequency-dependence of magnetic susceptibility, indicating presence of nanoparticles, has been also obtained in the sample No. 421 [7]).

The majority of compact glass coatings has high content of K, Cu and often more elements, like Zn or Rb. The composition little dependent on the rock forming the pebble reflects a contamination from local environment, probably dominated by material derived from plant biomass, like leaf litter, humus or organic sediment. Minor role of limonitic crusts in concentration of Zn and Cu is also possible (however, note that the glass sometimes covers ancient moss or lichen). As evidenced by crystallized minerals in glass, the cooling rate of external melt/glass coating on sample No. 420 was high but probably not extreme in comparison with industrial glasses (where similar crystals e.g. of diopside may form at temperatures well below solidus [8]).

The relatively young, little porous brown glass rich in Fe and probably also Ni is product of external material as well. This glass is very likely rich in superparamagnetic nanoparticles, too [7]. Schüssler [1] preferred origin from relatively easily melted pebbles of basic rocks, however our analyses of the sample 419 showed insufficient content of both Fe and Ni for such explanation. The brown glass is a promising material where accurate quantitative determination of Ni and, if possible, of platinum-group elements may bring evidence for presence of meteoritic matter.

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