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Post-impact alteration of impactites:
Ries crater, Germany



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LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following published papers, which are referred to in the text by their Roman numerals. The papers are reprinted by kind permission of the publishers.

- I **Muttik, N.**, Kirsimäe, K., Somelar, P., Osinski, G.R. (2008). Post-impact alteration of surficial suevites in Ries Crater, Germany: Hydrothermal modification or weathering processes? *Meteoritics and Planetary Science* 43, 1827–1840
- II **Muttik, N.**, Kirsimäe, K., Vennemann, T. W. (2010). Stable isotope composition of smectite at the Ries crater, Germany: Implications for hydrous alteration of impactites. *Earth and Planetary Science Letters*, 299, 190–195.
- III **Muttik, N.**, Kirsimäe, K., Newsom, H. E., Williams, L. B. (2011). Boron isotope composition of secondary smectite in suevites at the Ries crater, Germany: boron fractionation in weathering and hydrothermal processes. *Earth and Planetary Science Letters*, 310, 244–251.

Author's contribution

Paper I: The author was primarily responsible for data collection; X-ray diffraction and scanning electron microscope analysis, interpretation and synthesis of mineralogical analytical data and writing of the manuscript.

Paper II: The author was primarily responsible for fieldwork, whole-rock mineralogical analysis and smectite oxygen and hydrogen isotope analysis, interpretation of analytical results, synthesis of different analytical results and the writing of the manuscript.

Paper III: The author was responsible for data collection, analysis and interpretation of the boron isotopic composition of the secondary phases, and for writing the manuscript.

I. INTRODUCTION

Impact-induced hydrothermal activity (IHT) has been recognized as a typical post-impact phenomenon resulting in water rich targets from differential temperatures in the crater basement due to the post-shock residual heat remaining in rocks (Abramov and Kring, 2004, 2007; Jöeleht et al., 2005). Impact-induced hydrothermal activity is a well-known phenomenon that has been found at several terrestrial craters varying in size and target compositions (e.g., Koeberl et al., 1989; McCarville and Crossey, 1996; Ames et al., 1998; Sturkell et al., 1998; Naumov, 2002; Osinski et al., 2001, Osinski, 2005; Kirsimäe et al., 2002; Hagerty and Newsom, 2003; Hode et al., 2003; Versh et al., 2005); similar features have also been suggested for impacts on extraterrestrial planetary bodies (e.g., Allen et al., 1982).

Although the impact-induced hydrothermal activity has been studied extensively in last two decades, its structure and development is still poorly known (Naumov, 2005). The cooling of hot and/or moderately heated lithologies (e.g., impact melt rocks, melt glass-bearing breccias) in an impact crater is characterized by exponential temperature evolution with a fast temperature drop in the early stages of the cooling, followed by long and slow temperature decreases down to ambient conditions (Jöeleht et al., 2005).

The range of temperature variations, in space and time, results in specific secondary paragenetic mineral associations. Initial high temperature conditions when the temperature drop is the fastest are recorded mainly in mineral assemblages whose narrow equilibrium state allows rather precise mapping of the thermal aureole. The latest stages of the cooling occurs at temperatures below 300 °C, when temperatures last for exponentially longer times, results in a small number of mineral phases (mineral associations), typically characterized by clay mineral–zeolite–calcite–(pyrite) association (Naumov, 2005). This alteration is rock-dominated and dependent on target lithologies (Osinski, 2005). The impact-induced hydrothermal formations commonly exhibit two main zones of alteration: (1) moderate-temperature (chlorite – anhydrite zone) and (2) low-temperature (smectite(smectite-illite) – zeolite – carbonate zone) facies, which crystallization temperatures can be estimated from stability of hydrothermal phases in modern geothermal fields to be 350–180 and 200–50°C, respectively (Naumov, 2002; Kirsimäe et al., 2002).

The composition, structure and morphology of clay and zeolite phases depend on a number of environmental parameters, such as temperature, fluid composition/amount, pH, Eh etc. This makes them useful and important indicators for reconstructing any IHT environments. It is apparent, however, that clays and especially zeolites are thermodynamically metastable minerals, which are easily transformed by post-impact weathering and/or diagenetic and metamorphic alteration of impactites. As the result there is no understanding and consensus regarding low temperature IHT mineralization processes within crater rocks. Moreover, secondary clays and zeolites, as well as feldspars, can form directly under ambient conditions or diagenetically by devitrification of silicate glasses (e.g., Kastner and Siever, 1979; Sandler et al., 2004; Meunier, 2005).

The Ries impact crater (Fig. 1) is one of the most studied impact structures on Earth. Its impact origin was first recognized by Shoemaker and Chao in 1961 and since that time the geology and formation of the Ries crater has been addressed in numerous studies. Moreover, the Ries crater research over 5 decades has been fundamental with respect to many outstanding issues of planetary impact cratering research.

The Ries crater was also one of the first impact craters where possible impact induced hydrothermal alteration of impactites was suggested and described (Engelhardt, 1972; Salger, 1977; Stähle and Ottemann, 1977), although the alteration of impactites was already noticed earlier (e.g., Engelhardt, 1972). At the Ries crater, IHT has been addressed in detail by Newsom et al. (1986) and Osinski (2003, 2005), and Osinski et al. (2004). These studies have shown that hydrothermal alteration of the crater-fill suevites (polymict impact breccias – crater suevites, Engelhardt et al., 1995) is pervasive and characterized by argillic-type hydrothermal alteration with zeolitization; an early phase of K-metasomatism accompanied by minor albitization and chloritization at temperatures of approximately 200–300°C also occurred (Osinski, 2005). In contrast, the IHT mineralization in surficial suevites (fallout suevites, Engelhardt et al., 1995) at the Ries is not so well defined with the typical alteration product being montmorillonite-type clay mineralization at the expense of impact glasses (Newsom et al., 1986). Newsom et al. (1986) suggested that ~10–15 vol% of the montmorillonite is of hydrothermal origin in the groundmass of surficial suevites. However, Engelhardt (1997) and Osinski et al. (2004) reported that the suevite groundmass contains up to ~50 vol% of “clayey” material that is evidently a hydrous silicate (montmorillonite, according to Engelhardt 1997); however, the exact nature and origin of this clayey groundmass remained poorly constrained. Critical evaluation of earlier published data questions the interpretation of hydrothermal origin of crystalline montmorillonite in surficial suevites at Ries at all.

The aim of this thesis is:

- (1) firstly, to study the composition of the secondary phases within surficial and crater-fill suevite deposits from the Ries impact crater in order to understand their origin and alteration mechanism(s), using a detailed structural-mineralogical and geochemical characterization of alteration mineralogies, which would allow us to distinct the origin of these phases – i.e., low-temperature hydrothermal mineralization versus diagenetic devitrification and aerial-to-subaerial weathering of surficial suevites;
- (2) secondly, to examine the stable oxygen and hydrogen isotope composition of secondary clay minerals separated from the alteration zones of the surficial and crater filling suevites in order to understand the origin of the alteration, temperature distribution, and composition of the hydrothermal fluids;
- (3) thirdly, to constrain the origin and evolution of (geothermal) fluids in the Ries crater studying the boron isotope fractionation in surficial weathering and hydrothermal alteration processes in the secondary clay minerals of the surficial and crater-fill suevites.

2. GEOLOGICAL SETTING

The Ries impact crater in southern Germany is a 24-km diameter complex impact structure (Pohl et al., 1977) (Fig 1). It was formed about 14.59 ± 0.20 Ma ago (Buchner et al., 2010). Due to its young age and limited erosion, it is one of the best-preserved terrestrial complex impact craters on Earth (e.g., Hüttner and Schmidt-Kaler 1999; Buchner and Schmieder, 2009). It is also probably the best studied terrestrial impact structure. The crater is characterized by an almost circular and relatively flat inner basin of 12 km in diameter. The diameter of this ring coincides approximately with the maximum extent of the transient crater cavity (Wünnemann et al., 2005). The inner basin is surrounded by a crystalline ring of uplifted basement and an outer tectonic ridge representing a system of concentric normal faults (megablock zone) with a maximum extension of approximately 24 km in diameter (Pohl et al., 1977). The Ries impact occurred in a two-layer target consisting of flat-lying sequence of sedimentary limestones, sandstones, and shales of Triassic to Tertiary age that overlay Hercynian crystalline basement composed of gneisses, granites and amphibolites (Pohl et al., 1977; Graup, 1978). The largest proportion of shocked target material is in the suevites, the Ries crater's melt bearing breccias. This variously shocked, clastic material is embedded in a gray, fine-grained and (mostly) unshocked ground-mass (Graup, 1999).

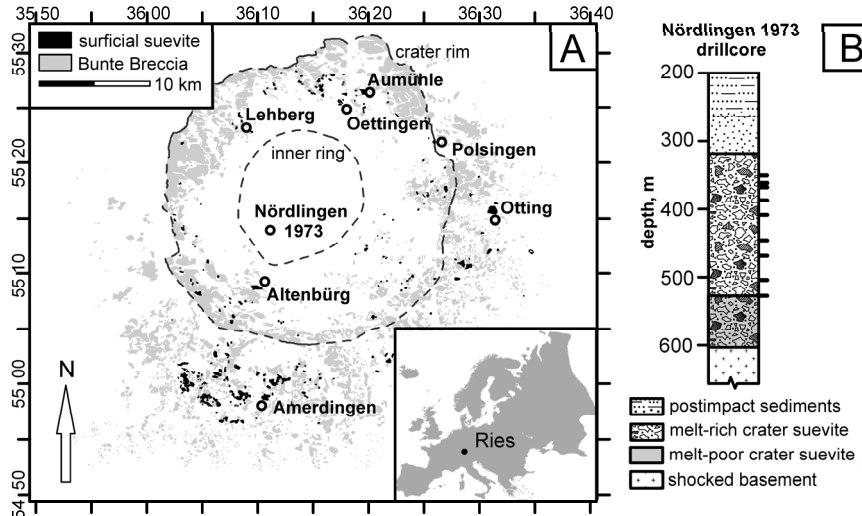


Figure 1. (A) Schematic map of the Ries crater, modified after Hüttner and Schmidt-Kaler (1999), with sample locations of surficial suevites investigated in this study. Coordinate system of the map is DHDN/3° Gauss Zone 2. (B) Simplified stratigraphy of the Nördlingen 1973 drill core (see Fig. 1a for location of drill site). Lines mark the sample depths investigated in this study.

The inner basin of the Ries crater is entirely formed in crystalline basement and filled by up to 400 m thick breccias overlain by ~400 m of post-impact lacustrine sediments (Pohl et al., 1977). No surface exposures exist of the crater-fill suevites, but the suevite layer is penetrated in approximately 270 m thickness in drillholes (Osinski, 2005). The outer zone of the structure is overlain by different types of proximal impactites (Engelhardt, 1990): (1) “Bunte Breccia,” a lithic polymict breccia containing clasts from basement rocks and sediments of the target; (2) polymict crystalline breccias, a lithic impact breccias with slightly to intensely shocked clasts from the deeper parts of the sedimentary cover and the Variscan crystalline basement; (3) surficial/fall-out suevites; and (4) coherent impact melt rocks. Surficial suevites, up to 25–30 m thick can be found in a distance of 22 km from the crater centre (Newsom et al., 1990; Engelhardt, 1990).

The suevite is considered a polymict impact breccia composed of a fine-grained groundmass containing both clastic and melt particles as well as larger clastic components of these phases (e.g., Stöffler and Grieve, 2007). The surficial suevites contain about 69 vol% components from the crystalline basement at all stages of shock metamorphism, 29 vol% shock-melted glassy inclusions, specifically vitreous and devitrified impact glass and about 2 vol% of matrix material dominated by montmorillonite type smectite (Engelhardt et al., 1995; Engelhardt, 1997). The surficial suevites are found in a large number of small isolated patches within the morphological rim and up to radial distances of up to 14 km beyond the rim to the south-southwest and east-northeast (Fig. 1). The thickness of the surface outcrops at the Ries is typically from few meters up to 25–30 m (Engelhardt, 1990; 1997); although substantial local variations are likely, given the presence of ~80 m of surficial suevite in the Wörnitzostheim drillhole (Engelhardt, 1990).

The suevites in the crater rim area have been divided into two units by Bringemeier (1994): (1) “main suevites” and (2) “basal suevites”. The “main suevites” comprise consolidated impact glass clast-rich blue-grey suevite, which constitutes the bulk of all suevite outcrops. The underlying “basal suevites” are poorly consolidated fine-grained suevite with minor content of glass and rock fragments (Bringemeier, 1994; Osinski et al., 2004). Overall, the surficial suevites consist of a matrix of 30–40 vol% montmorillonite-type smectite, 30–50 vol% glass particles, and 12–14 vol% rock fragments. The glass fragments showing various stages of devitrification are centimeter- to decimeter- sized, irregular, as well as, aerodynamically bomb-shaped pieces (Engelhardt et al., 1995; Engelhardt, 1997). The surficial suevite is lithologically different from so-called crater-fill suevite, which is only observed in drill cores. The crater-fill suevites form a massive (up to 400 m thick) layer in the crater depression below the post-impact crater lake sediments (Engelhardt et al., 1995). The crater suevite is a polymict breccia with lesser amount of glassy material as compared to surficial suevites (Engelhardt et al., 1995; Engelhardt, 1997). The crater fill suevite is composed of ~69 vol% clasts from crystalline rocks, 29 vol% of

mostly devitrified glass and about 2 vol% of matrix material dominated by montmorillonite-type smectites (Engelhardt and Graup, 1984).

The massive bodies of surficial suevites are dissected by numerous vertical pipe-like structures, up to some centimeters in diameter (Newsom et al., 1986). The pipe structures were considered as pathways for hydrothermal fluids and as the sites of intense alteration by Chao et al. (1978), and later reinterpreted as degassing pipes by Newsom et al. (1986). Within the pipes, the fine-grained matrix of the suevite has been removed, leaving the filling of coarser fragments that are coated with a light brown layer of undetermined Fe-rich oxide material (Newsom et al., 1986).

Engelhardt (1997) concluded that there is no coherent impact melt sheet at the Ries crater. Moreover, Stöffler (1977) suggested if there exists such a sheet or lens, deep-seated in the crater centre, it would be of minor size. However, Graup (1999) and Osinski (2004) suggest that isolated patches of so-called “red suevite” (e.g., at the Polsingen locality) can be considered as impact melt rock. This impactite overlies Bunte Breccia or megablocks within the crater and occurs as isolated bodies, with a lateral extent of approximately 10–100 m. These impact melt rocks comprise a reddish microscopic groundmass that contains lithic and mineral clasts (predominantly quartz) shocked to variable extent (Engelhardt, 1997; Pohl et al., 1977; Graup, 1999). The microcrystalline groundmass of impact melt rocks comprises alkali feldspar, plagioclase, quartz, and ilmenite, with interstices filled by either a fresh or devitrified glassy mesostasis (Osinski, 2004).

3. MATERIAL AND METHODS

The surficial suevite samples were collected from 6 outcrops within and around the Ries impact structure (see Fig. 1a). Crater-fill suevites were sampled from the Nördlingen 1973 drill core archived at the Center for Ries Crater and Impact Research (ZERIN), Nördlingen, Germany (Fig. 1b). Altogether, 46 different samples were studied.

Surficial suevite samples include glassy materials with no or limited visible alteration and highly altered glass nearly to completely, replaced with secondary clay phases. Collected samples also include wall rock of the degassing pipes. Material sampled from the Nördlingen 1973 drill core comprises low- and high-temperature suevite in intervals from 360 m to 525 m.

The mineralogical composition of samples was determined by X-ray diffraction (XRD) analysis, using Ni-filtered Cu-K α radiation on a DRON-3M diffractometer and/or Bruker D8 Advance diffractometer at the University of Tartu. The micromorphology of freshly broken interior surfaces of the most characteristic representative samples of suevite were examined with scanning electron microscopy (SEM), using Zeiss DSM 940 equipped with a SAMx SDD EDX detector. The interpretation of phases on secondary electron images was checked against the respective energy dispersive spectra.

The Green-Kelly Li-test according to Muravyov (1970) was applied to clay samples to distinguish the tetrahedrally substituted beidellite and octahedrally substituted montmorillonite. The infrared spectra of clay fractions were recorded using a Nicolet 6700 Fourier transform infrared spectroscopy (FTIR) at the University of Tartu; for additional quality check and for identification of montmorillonite-beidellite transition in the crater filling sequences according to Guisseau et al. (2007).

Clay minerals were separated by repeated centrifugation in distilled water to remove non-phyllsilicate constituents that can complicate the oxygen, hydrogen and boron isotope measurements. Any additional chemical pretreatment was avoided, as this may have adverse effects on the δD and $\delta^{11}B$ values (Hyeong and Capuano, 2000).

Stable oxygen and hydrogen isotope compositions of 18 samples were measured from clay separates of the suevite matrix at the Stable Isotope Laboratory at the University of Lausanne. Oxygen isotope compositions were measured on a Finnigan MAT 253 mass spectrometer and the hydrogen isotope composition using a Finnigan MAT Delta Plus XL mass spectrometer; according to a method adapted after Sharp et al. (2001). Replicate oxygen isotope analyses of the standards (Ls-1 – Lausanne quartz – and Kaolinite #17) yielded an average precision of $\pm 0.1\%$ for $\delta^{18}O$ values. The precision of the Kaolinite #17 and G1 biotite in-house standards for hydrogen isotope analyses was better than $\pm 2\%$.

B-isotopes and B-content of the $<2 \mu m$ clays of the 8 samples were measured using a Cameca 3f secondary ion mass spectrometer (SIMS); following the methods described by Hervig (1996) and Williams et al. (2001) at the Arizona State University. B-isotope values were corrected for instrumental mass

fractionation (IMF) by comparison with SIMS analyses of a reference material, Silver Hill Illite (Clay Minerals Society Source Clay, IMt-1). An average $\delta^{11}\text{B}$ value of $-9\text{‰} \pm 0.65$ was used for the IMt-1 illite (Williams et al., 2001). The standard for boron isotope ratio measurements is NBS SRM 951 boric acid, which has an $^{11}\text{B}/^{10}\text{B}$ ratio of 4.0437.

4. RESULTS

4.1. Mineralogical characterization of alteration mineralogies

The Ries surficial suevites comprise a fine-grained groundmass containing variably shocked mineral and lithic clasts from a wide range of target lithologies (e.g., Engelhardt and Graup, 1984, Engelhardt, 1990). Mineralogical analysis of the surficial suevites show, that the groundmass of the surficial suevite is mainly characterized by an assemblage of montmorillonite-type smectite, plagioclase, quartz, K-feldspar, and traces of zeolite (phillipsite) (Muttik et al., 2008 – PAPER I), this is in agreement with earlier studies (Osinski, 2005). There is some compositional variation in highly altered suevites where in addition to above-mentioned minerals also halloysite appears in remarkable amounts (up to 81 wt% of crystalline phases). The content of the rest of the minerals are below 5 wt%. In the bulk samples the mineral content is rather constant and does not show any clear trend (Muttik et al., 2008 – PAPER I).

In the crater-fill suevites, all primary impact-generated glasses have been completely replaced by various secondary minerals (cf., Stähle and Ottemann, 1977, Stöffler et al., 1977). In addition, the glasses contain only rare lithic and mineral clasts, in contrast to the surficial suevite glasses (Pohl et al., 1977). Earlier studies by Osinski (2005) have revealed the presence of several distinct alteration phases that vary distinctly with depth. The mineralogical composition of the crater-fill suevite is characterized by an assemblage of plagioclase, quartz, zeolites, K-feldspar and clay minerals. The composition of zeolites in the studied interval varies regularly with depth; low-silica zeolite (analcime) is the dominant zeolite recognized throughout the studied section. The high-silica zeolites (e.g., erionite) are found preferentially in the upper part of the crater-fill suevite deposits (Muttik et al., 2010 – PAPER II).

Clay minerals are ubiquitous throughout the studied surficial and crater-fill suevite sequences (Muttik et al., 2008 – PAPER I; Muttik et al., 2010 – PAPER II). Smectite is the most abundant clay mineral in surficial suevites. Structure refinement suggests that montmorillonite is of Al-Fe montmorillonite type. Low-charge octahedrally substituted dioctahedral Al-montmorillonite is a typical low temperature smectite, whereas the high temperature smectite is usually tetrahedrally substituted Al-beidellite (e.g., Meunier, 2005; Haymon and Kastner, 1986). The smectite nature of the clays was confirmed by applying the Green-Kelly Li-test (Muravyov, 1970) and by numerical modeling of montmorillonite structures by MLM2C code (Plançon and Drits, 2000), which indicates montmorillonite composition of smectitic clay in all samples. However, in some samples the Li-test points to the presence of some beidellitic layer-type clays as indicated by weak reversible expansion by after Li-treatment. Structural composition of smectite did not show any variance regardless to the location within the structure. Moreover, no signs of compositional or structural variation (e.g., illitization) were found between the possible fluid conduits and surrounding

rocks that would have induced by temperature gradients. However, in some samples the halloysite along with smectite was identified (Muttik et al., 2008 – PAPER I). It is to be noted that the majority of silicate impact glasses and mineral fragments are remarkably well preserved in the surficial suevites. Smectite coatings are abundant in all samples and have the same distinct morphology. The edges of flakes do not show any alteration or overgrowths, which would suggest the illitization of smectite (Fuente et al., 2002). The glass appears to have transformed directly to smectite through dissolution of glass to form smectite without forming amorphous precursor or primitive clays. Petrographic relations suggest that the smectite was apparently the first and the major mineral to form.

In crater-fill suevites, Fe-rich montmorillonite type smectite and mixed-layer illite-smectite were found to be the dominant alteration phase (Muttik et al., 2010 – PAPER II). No significant montmorillonite replacement with beidellite, was observed in the studied altered crater-fill suevite sequence using FTIR analysis. The mixed-layer illite-smectite accompanying the fully expandable smectite is characterized by random (R0) ordering with maximum of 5–10% of non-expandable layers. Micro-morphological analysis show, that smectite replaces partially to fully glass materials. In vesicular glass, the smectite flakes are arranged in honeycomb structures that fill or line the walls of existing cavities and pores or dissolution pits of the glass. Spatial relationships suggest that the smectite crystallization in the crater filling breccias predates precipitation of zeolites.

4.2. Oxygen and hydrogen isotopic composition of the clay fraction

The oxygen and hydrogen isotope composition of the smectite fraction from 17 samples of surficial and crater fill suevite were measured in order to elucidate the temperature of the fluids responsible for alteration of impact glass and primary silicate minerals and the formation of secondary clays in Ries crater. The significantly different oxygen isotope composition of secondary clay phases formed at the expense of glassy impact materials suggests significant hydrous alteration at large water/rock ratios and does not support the incipient devitrification mechanism of the impact glass transformation. The significant enrichment of the $\delta^{18}\text{O}$ and δD composition of the monomineral smectite fractions of the surficial suevites suggests low temperature origin of smectite. The $\delta^{18}\text{O}$ values of the smectite in surficial suevites range from 17 to 23‰. The hydrogen isotope compositions have a limited range between the sampled outcrops, with a mean δD value of $-97 \pm 6\text{‰}$. Smectite $\delta^{18}\text{O}$ and δD values in crater-fill suevite clay fraction samples, however, range from 8‰ to 15‰ and -33‰ to -99‰ , respectively. For the crater-fill suevites, however, a trend towards lower $\delta^{18}\text{O}$ values and higher δD values is evident. The $\delta^{18}\text{O}$ values

decrease from 14 ‰ at 360 m to 8‰ at 525 m depth, while δD values increase from -96 ‰ at 360 m depth to -52 ‰ at 525 m.

The oxygen stable isotope composition of fluids, assuming that the smectite was equilibrated with the alteration fluids, indicates $\delta^{18}O$ values of fluid averaging -6.9 ± 1.1 ‰ and -5.9 ± 2.3 ‰ in surficial and crater filling suevites, respectively (Muttik et al., 2010 – PAPER II). This range of the fluid oxygen isotope values calculated from composition of smectite coincides with the variation of $\delta^{18}O$ of meteoric water (-7 ‰ to -5.9 ‰) in the Ries area, since the formation of the impact crater (e.g., Tütken et al., 2006).

4.3. Boron isotopic composition of the secondary phases

The B content of the 8 samples of the secondary clay phases from Ries crater suvites were measured, expecting to see changes similar to the oxygen and hydrogen analysis (Muttik et al., 2011 – PAPER III).

Analysis showed the significant difference between the boron isotopic composition of the surficial and crater filling samples. The average $\delta^{11}B$ values for the smectite from the four areas of the surficial suevite samples analyzed ranged from -26.3 ± 1.9 ‰ to -22.7 ± 1.5 ‰, while the average $\delta^{11}B$ values of smectite in crater filling suevites were -4.07 ‰, except the deepest sample R09, which also shows a very low boron isotopic values (-21.8 ‰). After the exchangeable B was removed by NH_4Cl exchange treatment, the B isotopic composition of smectite in surficial and crater fill suevites did not change significantly. The average $\delta^{11}B$ values before and after the NH_4Cl exchange process are similar.

The boron isotopic signature of the surficial samples show much more negative values than anticipated for detrital sediments (Ishikawa and Nakamura, 1993; Spivack et al., 1987), for silicate rocks (Palmer and Swihart, 1996 and references therein) or average isotopic composition of continental crust (-7 ‰, Chaussidon and Albarède, 1992).

5. DISCUSSION

5.1. Hydrothermal mineralization or aerial-to-subaerial weathering origin of secondary clays in surficial suevites

Hydrothermal alteration in active hydrothermal systems is typically characterized by a zonal distribution of alteration and directional distribution of altered minerals that is principally related to mass transfer between minerals and hydrothermal solutions as temperature decreases when the hydrothermal solutions pass through rock (Helgeson, 1979). The distance between the high-temperature and low-temperature zones is a factor of the vertical thermal gradient at a given place (Inoue, 1995; Meunier, 2005). Importantly, as the number of variables in a hydrothermal system increases, a greater variety of clay minerals can be expected to form under different hydrothermal environments (Inoue, 1995). The same spatial structure and specific alteration gradients of the hydrothermal alteration are described for IHT systems. There, the most intense alteration with thermal gradients in order of $100\text{ }^{\circ}\text{C km}^{-1}$ occurs within the hottest central parts of an impact structure (Naumov, 2005; Masaitis and Naumov 1993; Versh et al., 2005).

In contrast to hydrothermal alteration, weathering of rocks occurs under virtually constant temperature-pressure conditions at the Earth's surface. As a consequence, the most important factor of weathering is the composition of the acting fluid; whereas temperature and especially pressure variation are practically negligible, at least in short term (Meunier, 2005). The variability of secondary phases (clays) generated during weathering is a function of the minerals present in the rock, and the number of coexisting secondary phases in a system is much less (frequently monovariant) than in hydrothermal environments.

The clay minerals in the groundmass of the Ries suevites have been recognized since the early 1970's (e.g., Engelhardt, 1972; Chao et al., 1978; Newsom et al., 1986; Osinski, 2005). It is generally accepted that these clays were formed by post-impact hydrothermal alteration of impact-generated glasses and/or finely comminuted crystalline basement material (Engelhardt and Garup, 1984; Newsom et al., 1986; Osinski, 2005).

Hydrothermal alteration in crater-fill suevites is well defined. Osinski (2005) suggests that the major heat source for the Ries hydrothermal system was the suevite unit themselves and that the hydrothermal alteration of crater-fill suevites is pervasive in nature and comprises several distinct alteration phases that vary with depth. In crater-fill suevites an argillic-type of hydrothermal alteration (predominantly montmorillonite, saponite, and illite) and K-metasomatism associated with zeolitization (predominantly analcite, erionite, and clinoptilolite) can be observed (Osinski, 2003; 2005; Osinski et al., 2004). The hydrothermal alteration within the crater-fill suevites was estimated from mineral associations and comparisons with studies at other craters occurring at temperatures of approximately 200-300 °C (Osinski, 2005). The predominance

of alkali and calcic zeolites is indicative of weakly alkaline hydrothermal solutions, which is typical for impact-induced hydrothermal systems in general (Naumov 2002, 2005; Osinski 2005). The source of the fluids for the Ries hydrothermal system was likely a combination of surface (meteoric) waters that percolated down from the overlying crater lake and groundwater that flowed in from the surrounding country rocks into the hydrostatic space created by the impact event (Osinski 2005).

In contrast to the crater-fill suevites, as this work shows, the supposed impact-induced hydrothermal alteration within surficial suevites is limited and typically restricted to montmorillonite-type clay mineralization and minor zeolite (mainly phillipsite) deposition within cavities and fractures (cf., Newsom et al., 1986; Osinski, 2005; Osinski et al., 2004). The lack of illite-smectite type mixed-layering in the montmorillonite constrains the main alteration event in the surficial suevite to temperatures <100–130°C; these are consistent with alteration after temperatures have fallen below the boiling point and liquid water could then be present (Newsom et al., 1986).

The absence of significant hydrothermal alteration in surficial suevites is further confirmed by textural relationships. Graup (1999) pointed out that majority of the glasses are unaltered and all extremely delicate textures of primary silicate impact-melt glass have well preserved, ruling out at least large-scale replacement processes. Moreover, only a limited number of alteration products (montmorillonite, halloysite, zeolite) have been found.

Engelhardt (1972) noted that pipe like structures (“vertical chimneys”), which intersect the suevite in several suevite outcrops, indicate the degassing of the breccia and have been considered as pathways for hydrothermal fluids and as the sites of intense alteration (Chao et al., 1978). However, Newsom et al. (1986) suggested that the degassing pipes have probably remained mostly dry since the original degassing event occurred, indicating that the suevite was in the unsaturated or vadose zone during the main period of the hydrothermal alteration. Results of this study show that there is no evidence of hydrothermal clay mineral alteration within the degassing pipes. There is no variation in clay mineral composition between internal surface layers of pipes and at a distance from the pipe. In all cases the dominant secondary phase is the same Al-Fe type montmorillonite. However, the internal surfaces of degassing pipes are frequently over-/intergrown with calcite, which paragenetically postdates the clay phases.

The abundant presence of smectite in surficial suevites at the Ries crater indicates that the alteration in these deposits proceeded at relatively low temperatures. Smectite is thermally a metastable phase and its conversion to illite through mixed-layer illite-smectite takes place over a broad temperature interval of 70–150 °C. The temperature interval varies as function of kinetically controlled processes of the reaction progress (Inoue et al. 1992; Essene and Peacor 1995). In addition, a low temperature (<100 °C) origin of this mineral is indicated by its composition – octahedrally substituted Al-Fe montmorillonite –

whereas the high temperature smectites are typically tetrahedrally substituted beidellites (Inoue et al. 1992).

Our results suggest that in the surficial suevites the glass appears to have transformed to smectite through dissolution of glass without forming amorphous precursor or primitive clays. Randomly oriented montmorillonite-type smectite flakes fill or coat the walls of existing round cavities and pores or that forming during the dissolution of the glass. The similar appearance of the smectite in different parts of the rock and at different localities indicates that precipitation of smectite has not been controlled by hydrothermal fluids, but rather by slowly percolating meteoritic waters.

In addition to smectite, alteration of the suevite glass was accompanied by formation of minor halloysite. The formation of halloysite further confirms the importance of low temperature hydrous weathering. The chemical composition of solutions in weathering is determined by the properties of meteoric fluid that essentially contain CO₂ and accordingly are acidic and also undersaturated. Composition of hydrothermal fluids, however, depends upon the composition of the target rocks (e.g., crystalline versus sedimentary, mafic versus acidic rocks) present at the impact site as well as on the fluid source (Naumov 2005).

5.2. Temperature distribution and composition of the aqueous (hydrothermal) fluids

The different formation temperature of the surficial and crater fill suevites is evident from the estimated fluid temperatures using smectite stable isotope geothermometry by Delgado and Reyes (1996), which suggests that the smectite precipitated in equilibrium with meteoric fluid at temperatures averaging from 16 ± 5 °C, with exception of the sample R 32 from Amerdingen locality with a calculated temperature of 31 °C. This estimate is similar to the variation of mean annual air temperature (MAT) of 19 ± 4 °C in the Middle Miocene (Tütken et al., 2006), but higher than modern temperatures of 8–9 °C. The variation in calculated MAT and $\delta^{18}\text{O}$ of water may reflect the large time span of weathering represented by the surface clay minerals, which started directly after the impact and is still ongoing today. Moreover, using the oxygen isotope fractionation equation between smectite and water (Sheppard and Gilg, 1996) and present-day temperatures (8–9 °C), the calculated $\delta^{18}\text{O}$ values of fluid average at $-6.9 \pm 1.05\%$, which coincides with $\delta^{18}\text{O}$ values of modern meteoric water (-7% , Rozanski et al., 1993) in this area. The fluid composition also agrees with the paleoclimatological reconstruction of $\delta^{18}\text{O}$ values of meteoric water in the Steinheim basin, which is a small impact structure, most probably formed together with Ries crater at a distance of 50 km.

In crater fill suevites the estimated temperatures increase with the depth from ~ 40 °C at 360 m depth to 110 °C at 525 m depth. In contrast, present day temperatures in the Nördlingen 1973 dill-hole increase in this depth interval monotonously from 34 °C to 40 °C (Popov et al., 2003). The elevated formation

temperatures of the smectite point to hydrothermal origin probably during the cooling of the Ries impact structure. If we assume that smectite mineralization in crater filling suevites was equilibrated with hydrothermal fluids, then the calculated $\delta^{18}\text{O}$ of fluid was $-5.90 \pm 2.31\text{‰}$. This value coincides with the range of $\delta^{18}\text{O}$ of meteoric water (-7‰ to -5.9‰) reported for this area, since the formation of the crater (Tütken et al., 2006); suggesting that the hydrothermal system was fed by the water of meteoric origin.

Interestingly, the temperatures of the hydrothermal fluid estimated from the smectite minerals are 80–180 °C lower than estimated from mineral associations earlier (e.g., Osinski 2005) suggesting that the smectite formation occurred during the latest phase of the impact cooling. Moreover, the calculated fluid temperatures increase monotonously with the depth, though earlier studies of the Ries have described an inverted structure of the post-impact hydrothermal alteration with high temperature K-metasomatic alteration, albitization, and chloritization restricted to upper parts of the crater filling suevitic layer (e.g., Osinski, 2005). Nevertheless, the mineral paragenesis of smectite and zeolite minerals suggest that the smectite was not the last mineral phase forming in Ries hydrothermal systems and it was followed by widespread analcime precipitation probably at temperatures close to ambient.

The normal structure of the hydrothermal system in the Ries crater-fill suevites is supported by the observed zoning of zeolite mineralization. The temperature stability of smectite and clinoptilolite in association with erionite and phillipsite/chabazite in the upper part of the crater-fill breccia sequence, denotes maximum temperatures of about 100 °C, and smectite – analcime association temperatures above 100 °C (e.g., Bish and Aronson, 1993; Inoue et al., 2004). The analcime – albitite transition in the lower part of the melt-rich crater filling breccias (Osinski, 2005), indicates temperatures in excess of 175 °C (Bish and Aronson, 1993). The stability of zeolite minerals, however, can also be controlled by chemical variables of the fluid (e.g., Si/Al ratio, activity of alkalis, pH) as well as fluid/rock ratio rather than only temperature (Birsoy, 2002; Chipera and Bish, 1997).

The inverted vertical structure of alteration can be understood in terms of a two-stage post-impact hydrothermal alteration within the crater filling suevites. The initial high-temperature alteration stage occurred at conditions, probably, close to critical point of water and is characterized by K-metasomatism and chloritization. This stage was driven by the heat of the hot suevite. During later stages of cooling, the hydrothermal convection was driven by the thermal gradient due to the uplifted basement (McCarville et al., 1996), resulting in the normal vertical structure of the hydrothermal alteration at medium to low (<300 °C) temperatures that overprinted the earlier high-temperature mineralization.

Our results show that dominant alteration (hydrous silicates as smectite type clay minerals and zeolites) occupying the largest volume of rock, forms in the latest phase of the impact cooling at temperatures <100–150 °C. Cooling of the various lithologies in an impact structure is characterized by exponential

evolution with a fast temperature drop in the beginning; followed by a long and slow temperature decrease, down to ambient conditions (Jöeleht et al., 2005; Versh et al., 2005; Abramov and Kring, 2007). Consequently, in the latest stages of the cooling, the now lowered, yet still elevated temperatures last for exponentially longer times and the low-temperature hydrothermal mineral associations prevail in the altered rocks.

5.3. The origin and evolution of (geothermal) fluids in the Ries crater

Several recent studies have highlighted the potential utility of boron isotope ratio as a tracer for fluid-rock interactions (Hervig et al., 2002; Williams and Hervig, 2002; Williams et al., 2001; Williams and Hervig, 2005; Deyhle and Kopf, 2005; Gonfiantini and Pennisi, 2006; Pennisi et al., 2009). The fractionation of B isotopes during such processes is due to the preference of each B isotope for a different coordination state; tetrahedral coordination for ^{10}B , trigonal coordination for ^{11}B and ionic radii (Palmer and Swihart, 1996). Boron is incorporated into the clay mineral structure in tetrahedral sites and can also be adsorb to clay surfaces, including those in the clay interlayers (Williams and Hervig, 2002; Williams et al., 2001). B adsorption on clays causes a preferential ^{10}B uptake related to the coordination change of B from trigonal to tetrahedral on the clay surfaces (Palmer et al., 1987; Palmer and Swihart, 1996). This fractionation of B isotopes between trigonal and tetrahedral coordination during fluid-rock interactions has been considered temperature dependent and insensitive to mineral composition (Williams et al., 2001; Hervig et al., 2002). Moreover, the B fractionation can be used to study other parameters, including B concentration in solution, pH, duration of interaction between clay and solution, and pressure and salinity (Deyhle and Kopf, 2005; Klochko et al., 2006). The boron concentration and isotopic signature in different geochemical reservoirs (e.g. mantle, oceanic and continental crust, seawater, sediments) span an extremely wide range from <0.1 to >100 ppm B and from $\delta^{11}\text{B}$ of about -30‰ to $\delta^{11}\text{B}$ of about $+60\text{‰}$ (e.g., Barth, 1993; Bebout et al., 1993). These geochemical characteristics make boron an excellent tracer for modeling geochemical cycles and determining different sources in fluid-mediated and fluid-dominated processes. Particularly, the large isotopic fractionation between alteration fluids and mineral phases makes B a sensitive indicator of weathering reactions and specifically to the budget between mineral dissolution and precipitation of secondary phases (Cividini et al., 2010).

Secondary smectite in altered suevites originates mostly from devitrification/recrystallization of impact glass. Chaussidon and Koeberl (1995) have shown that the boron isotopic composition of tektites and impact glasses from world-wide occurrences (Australasian, North American, and Ivory Coast strewn fields and Aouelloul and Darwin craters) have a rather limited range of $\delta^{11}\text{B}$, with an average of $+2.7\text{‰} \pm 1.5\text{‰}$ and are similar to those of surface

continental source rocks. Koeberl (1986) reported B concentration of 19 ppm in tektite glasses (moldavites) derived from the formation of the Ries crater, which agrees with the range of boron variation in studied smectite samples (25±16 ppm).

Typically the smectite from altered volcanic ash or weathered continental sources is expected to have an initial B-isotopic composition around 0‰ assuming that alteration processes did not add B into the system (Leeman and Sisson, 1996; Palmer and Swihart, 1996). Isotopic fractionation of B in smectitic clays starts during the diagenetic recrystallization process of the illitization of smectite, when B substitutes for Si in the authigenic illite tetrahedral sites (Williams and Hervig, 2002). A large isotopic fractionation (−31‰) between trigonally coordinated B in fluid (pH<8) and tetrahedral bonds formed by mineral surface adsorption can occur at 25°C (e.g., Palmer et al., 1992). However, pretreatment with mannitol and cation exchange with NH₄Cl should have removed adsorbed and interlayer boron. Depleted δ¹¹B in smectite in Ries surficial samples may represent B incorporated into the mineral structure by replacing Si in tetrahedral positions during the growth of the authigenic smectite. This agrees with observations of seawater alteration (including serpentinization) of oceanic basalts, which show that phyllosilicates can incorporate significant amounts of boron in crystal structure at low to moderate temperatures (Früh-Green et al., 2004; Savov et al., 2006; Boschi et al., 2008).

The boron isotope fractionation between (secondary) mineral phases and fluids depends significantly on the temperature, pH and, to a lesser degree, salinity (ionic strength) of the solutions (e.g., Hershey et al., 1986; Liu and Tossell, 2005). B isotope fractionation between fluid and mica-like phyllosilicate phases can be modeled as a function of temperature, pH and salinity/ionic strength (e.g., Pagani et al., 2005; Boschi et al., 2008; Pennisi et al., 2009; Vils et al., 2009).

The coordination of dissolved B-species is pH dependent, with predominately trigonal coordination at neutral to low pH and tetrahedral coordination at higher pH (Hemming and Hanson, 1992; Palmer and Swihart, 1996). In the pH range of meteoric water (pH <7) dominant species, composed of >95% dissolved boron, are trigonally coordinated B(OH)₃ whereas the boron is incorporated into clays in tetrahedral coordination either by surface/interlayer adsorption or substitution to tetrahedrally coordinated Si. In this pH range (<7), the fractionation is not (at least significantly) influenced by ionic concentration of the fluid and mineral-water fractionation is mainly controlled by temperature (Williams et al., 2007). In this sense, the comparison of the modeled δ¹¹B variation and the range of measured boron isotope compositions in surficial suevites suggest the isotope exchange at low temperatures, as evident from (very) low negative δ¹¹B values of the smectite, and pH range up to maximum 8 assuming saline water or 8.5 assuming fresh water composition of the fluids. The mica-like mineral-water fractionation (*sensu* Liu and Tossell, 2005) is insensitive to pH variation up to values of 7–8. Therefore, we suggest that the alteration of fall-out suevites in a slightly acidic environment (percolation of

meteoric water) is well justified and consistent with the low temperature (meteoric) weathering origin of the smectite.

Relatively low pH of interstitial waters is also indicated by limited occurrence of authigenic quartz and zeolite minerals. Zeolites have been reported in surficial suevites by earlier authors (e.g., Pfannschmidt 1985; Osinski 2005), but their occurrence is scarce in the samples studied here, only one sample (RS 11 – Muttik et al., 2008 – PAPER I) contain traces amount of zeolite. The pH is the most important control on zeolitization, which requires neutral to alkaline conditions and sufficient Si and alkali activity in the fluid (Hey 1978). These conditions were most probably not met in most part of the surficial suevites in the crater interior.

The less negative $\delta^{11}\text{B}$ values of the smectite in crater filling suevites indicates precipitation at higher temperatures and/or at elevated pH (>8–9), except the deepest sample R09. There is minimal isotopic fractionation where there is no coordination change (Hervig et al., 2002), therefore at progressively higher temperatures and pH values above the $\text{p}K_B$ (which is a temperature dependent parameter) the mineral $\delta^{11}\text{B}$ would reflect the water composition without significant fractionation. The comparison of the model and measured B-isotope values in crater fill suevites suggest pH >9 of the alteration fluid. The elevated pH of the fluids in crater filling suevites is possibly related to the effective removal of the available H^+ ions in hydrothermal fluid through anion hydrolysis of primary silicates, which agrees with the estimated geochemical environment of the authigenic alkali feldspar and clay-zeolite-carbonate hydrothermal mineral assemblage in crater fill sequence (Osinski, 2005). The predominance of alkali and calcic zeolites is indicative of weakly alkaline hydrothermal solutions, which is typical for impact-induced hydrothermal systems in general (Naumov 2002, 2005; Osinski 2005).

The general B behavior during the weathering of rock shows B accumulation in secondary phases with a strong preference for the light isotope (e.g., Cividini et al., 2010; Rose et al., 2000). However, it is unclear to what extent the fluid-rock/mineral isotope-exchange under low temperature weathering takes place and whether the equilibrium between percolating meteoric water and secondary mineral could be achieved. Interestingly, the δD and $\delta^{11}\text{B}$ composition of studied surficial smectites plots on a line parallel to Boron Meteoric Line (BML, Rose-Koga et al., 2006), with nearly the same slope of 2.8 for surficial smectite and 2.6 for the BML. The slope of the BML, as well as for Meteoric Water Line (Craig and Gordon, 1965), is considered insensitive to variations in mean air temperature of the surface (Rose-Koga et al., 2006) and the shift (interception) of the line would be caused by systematic exchange of the isotopes during the crystallization of mineral phases. By analogy to δD and $\delta^{18}\text{O}$ fractionation (e.g., Sheppard and Gilg, 1996) this would indicate that the smectite in surficial suevites precipitated in equilibrium with the boron and hydrogen isotopic composition (at given temperatures) in the meteoric water from precipitation that percolated through the system. Moreover, the calculated $\delta^{11}\text{B}$ composition of the fluids for surficial suevites ($7.5 \pm 1.6\text{‰}$) agrees with the B isotopic composition

of continental rain at distance from sea and/or high latitudes/ altitudes (e.g., Rose-Koga et al., 2006), which is applicable to the location of the Ries crater. Large fractionation of the B isotopes between fluid and smectite formed in fall-out suevite is then consistent with the B isotope composition in meteoritic water (Rose-Koga et al., 2006) by +30‰ to +32‰ during incorporation of boron into the clay structure at 20°C. However, we must consider that the typical boron concentrations in precipitation water (0.1–1 ppb, Rose-Koga et al., 2006) are five to four orders of magnitude less than in rocks (~19 ppm in the Ries' suevites) and a large amount of water and strong leaching of original and preferential (cumulative) take up of precipitation water boron would be needed for this equilibration. A simple fluid-rock interaction model (Banner and Hanson, 1990; Jacobsen and Kaufman, 1999) suggests that isotopic equilibration of rock (concentration of B 19 ppm, $\delta^{11}\text{B}$ 3‰) with precipitation water (concentration of B 1 ppb, $\delta^{11}\text{B}$ 7.5‰) at 20 °C, assuming boron water-mineral fractionation –32‰, calculated according to equation of Williams et al. (2007) would require water to rock ratio of >1,000,000 in a closed system and ~100,000 in an open system interaction. The mean annual precipitation in the Bavarian pre-Alp area varies between 600–1200 mm·yr⁻¹ (Schwarb et al., 2001). If we assume a mean precipitation 800 mm·yr⁻¹ over the post-impact period and consider that approximately half of that is evaporated, then the amount of the water infiltrating into the rock would amount to 400 mm·yr⁻¹. Thicknesses of the surficial suevite deposits are between 10-20 m (Engelhardt, 1972), but at least 50 m thick deposits could be considered, accounting the post-impact erosion. The (open/interconnected) porosity values of the suevite vary between 20-34% (Engelhardt, 1972). If we assume minimum porosity 20% of the suevite rock, then the water to rock ratio of about 100,000 what is required to achieve the complete isotopic exchange in an open system, is reached in 10 million years. The age of the Ries crater is 14.59±0.20 Ma (Buchner et al., 2010), which means that it is quite possible for the smectite in surficial suevites to be equilibrated with the boron and hydrogen isotopic composition of the percolating meteoric water and the B- and H-isotopic composition of secondary clay phases could be used to evaluate the (past) surficial environments. Moreover, this low temperature B- and H-isotope exchange between fluid and secondary clay phases under strongly leaching weathering conditions in equilibrium with precipitation water can explain the observed large fractionation of $\delta^{11}\text{B}$ values (+40–45‰) observed in non-hydrothermally impacted rivers in Guadeloupe volcanic terrains, Lesser Antilles (Louvat et al., 2011).

6. CONCLUSIONS

The 24-km diameter Ries crater, in Germany, is one of the best-preserved terrestrial complex craters; providing a good opportunity to study the evolution of the post-impact cooling in impact structures. The mineralogical alteration of impactites and characteristics of aqueous alteration fluids in the Ries crater were studied. The mineralogical, geochemical and stable isotope studies suggest a different origin of alteration and temperature distribution for the surficial and crater filling melt-bearing impact breccias.

The mineral composition of altered surficial suevites is characterized by an assemblage of montmorillonite-type smectite, plagioclase, quartz, and K-feldspar, and does not show any variation between different locations. However, highly altered suevites were found to contain halloysite, in remarkable amounts (up to 81 wt% of crystalline phases).

Clay fraction analyses show that the dominant alteration phase is smectite with a composition corresponding to dioctahedral Al-Fe montmorillonite, which is a typical low temperature smectite, pointing to weathering as the major reason for alteration without evidence of hydrothermal modification. The low temperature hydrous devitrification of the impact glasses is verified by the occurrence of halloysite in highly altered suevites. Smectite coating is abundant in different parts of the surficial suevites and there is no compositional variation between internal surface layers of pipes and at distance from the pipes.

Low-temperature alteration of surficial suevites is also confirmed by stable oxygen and hydrogen isotopic composition analysis of secondary smectite clay fraction. The estimated fluid temperatures, using data derived by δD and $\delta^{18}O$ fractionation, suggest smectite precipitation in surficial breccias in equilibrium with meteoric fluids at temperatures 16 ± 5 °C, this estimate is in agreement with the variation of mean annual air temperature in the last 15 Ma of the area. The fluid oxygen isotope values calculated from composition of smectite average at -6.9 ± 1.05 ‰ in surficial suevites, which coincides with the variation of $\delta^{18}O$ of meteoric water (-7 ‰ to -5.9 ‰) in the Ries area, since the formation of the meteorite structure.

In contrast to the surficial suevites, the alteration within crater-fill suevites is characterized by argillic-type of hydrothermal alteration with zeolitization; an early phase of K-metasomatism accompanied by minor albitization and chloritization occurred at temperatures of approximately 200–300 °C (Osinski, 2005). Different origin of alteration and temperature distribution for the crater filling suevites compared to surficial suevites is supported by our mineralogical investigations and oxygen and hydrogen isotope analysis. The stable isotope composition of smectite in crater-fill suevites suggest the alteration in the crater filling sequence in the presence of meteoric water-dominated fluid circulation at temperatures of 40 to 110 °C, indicating that the temperatures of the hydrothermal fluid estimated from the smectite minerals are 80–180 °C lower that estimated from mineral assemblages (Osinski, 2005).

Earlier studies of the Ries crater and some other terrestrial impact structures have described an inverted structure of the post-impact hydrothermal alteration with high temperature alteration restricted to upper parts of the crater filling suevite layer (e.g., Osinski, 2005; Naumov, 2005). Our results show the normal structure of a hydrothermal system with the fluid temperature increasing with increasing depth through the suevite sequence, suggesting that the inverted structure of hydrothermal systems probably represents only the initial configuration of the thermal anomaly in a crater, however it may be replaced with a dominant normal hydrothermal convection in the crater proper during the post-impact cooling progress.

Boron isotopic analyses of smectite in the surficial and crater-fill suevites were carried out to constrain the origin and evolution of the (geothermal) fluids that were involved in the formation of alteration mineralogy. Measured and calculated/modeled $\delta^{11}\text{B}$ composition indicate that, now visible, alteration of surficial suevites occurred at lower temperatures, lower pH and in slightly acidic environment (percolation of meteoric water), which is consistent with the mineralogical and oxygen and hydrogen studies, showing that the smectite in surficial suevites precipitated in equilibrium with meteoritic fluids (Muttik et al., 2008 – PAPER I; Muttik et al., 2010 – PAPER II). Interestingly, our results show that the δD and $\delta^{11}\text{B}$ composition of secondary smectites in surficial suevites indicate the smectite precipitation in equilibrium with the boron and hydrogen isotopic composition in the meteoric water that percolated through the system and the B- and H-isotopic composition of secondary clay phases could be used to evaluate the (past) surficial environments.

The modeled $\delta^{11}\text{B}$ composition of crater-fill suevites, however, indicate that the alteration in the crater-fill suevites took place at higher temperatures and/or at elevated pH (>8–9) than in surficial suevites. The elevated pH of the alteration fluids in crater filling suevites is possibly related to the effective removal of the available H^+ ions in hydrothermal fluid (evolved meteoric water) through anion hydrolysis of impact glass and primary silicates. However, future boron isotope work of different size fractions of clay phases may advance our knowledge of the changes in the fluid system during crystal growth, allowing us to determine whether and how much the hydrothermal system was influenced by the overlying evaporative (meso-hyperhaline) saline shallow-water crater lake.

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SUMMARY IN ESTONIAN

Impaktkivimite sekundaarne muutumine hüdrotermaalsetes ja diageneesi-murenemise protsessides: Ries'i meteoriidikraater, Saksamaa

Lõuna-Saksamaal paiknev ligikaudu 24-kilomeetrise läbimõõduga Reis'i meteoriidikraater (14,3–14,5 Ma) on üks paremini säilinud impaktstruktuure, olles heaks mudelstruktuuriks impakti järgsete protsesside uurimisel. Riesi kraater on ühtlasi ka üks esimesi impaktstruktuure, kus on kirjeldatud ja oletatud impakt-indutseeritud hüdrotermaalset mineralisatsiooni. Hüdrotermaalset muutust on seostatud ennekõike süveviitse kompleksiga ning on kirjeldatud detailsemalt Newsom et al. (1986), Osinski (2003,2004) ja Osinski et al (2004) töödes.

Kraatrit täitvate süveviitide hüdrotermaalseid muutuseid/ilminguid iseloomustab sekundaarne savimineralisatsioon ja teoliidistumine, millega kaasneb varajane K-metasomatism koos albitiseerumise ning kloritiseerumise ilmingutega temperatuuridel ~200–300°C (Osinski 2005). Samas pole pindmiste süveviitide hüdrotermaalne mineralisatsioon nii selgelt märgatav/eristatav ning seda on seostatud impaktklaasi muutumisel tekkima hakanud montmorilloniidi tüüpi savifaasiga (Newsom et al 1986). Näiteks moodustab Newsom et al. (1986) andmetel Ries'i kraatri pindmiste süveviitide põhimassist vähem kui 10–15vol% ainsa identifitseeritava faasina hüdrotermaalse tekkega smektiitne savimineraal montmorilloniit. Samas leiavad Osinski et al. (2004) ja Osinski (2005), et sama süveviidi põhimass sisaldab lisaks nimetatule veel kuni 50 vol% savikat massi, mis on hüdratiseerunud silikaatse koostisega. Kui Ries'i süveviidid sisaldavad vaid <10–15vol% hüdrotermaalset smektiiti (montmorilloniiti), siis milline on ülejäänud savika põhimassi olemus ja teke? Need tulemused seavad küsimärgi alla ka varem identifitseeritud montmorilloniidi hüdrotermaalse päritolu.

Mineraloogilised tulemused näitavad, et Riesi kraatri pindmiste süveviitide mineraalses koostises domineerivad peamise faasina montmorilloniidi tüüpi smektiit, plagioklass, kvarts ja K-päevakivi. Mõningast mineraalide sisalduse erinevust võib märgata tugevalt muutunud pindmistes süveviitides, kus lisaks smektiidile ilmnis märgatavas koguses sekundaarse faasina ka savimineraal halluasiit (kuni 81 wt%). Ülejäänud mineraalide sisaldus jäi alla 5 wt%-i. Savimineraalide detailne mineraloogiline analüüs näitab, et domineerivaks sekundaarseks faasiks on montmorilloniidi tüüpi smektiit, mis struktuurianalüüside järgi on praktiliselt puhas madalatemperatuuriline Al-Fe montmorilloniit.

Sellist tüüpi montmorilloniit ei ole tavaliselt hüdrotermaalset päritolu, vaid on seotud madalatemperatuurilise hüdrofüütilise murenemisega (nt. Meunier 2005). Veelgi enam – valdavalt murenemise tüüpi muutumist kinnitab ka tüüpilise kõrge kivimi/vee suhtega halluasiidi esinemine koos montmorilloniidiga kõige kõrgema muutumisastmega süveviitides. Samuti ei täheldatud montmorilloniidi struktuurse koostise varieeruvust süveviitse kompleksi erinevates osades, ega ka võimalikke hüdrotermaalseid fluide juhtinud lõhedes (degaseerimis-kanalites) ning nende ümbriskivimites, mis on vastupidine eeldatud hüdrotermaalsele

geneeesile. Antud uurimuse tulemused näitavad, et hüdrotermaalsete protsesside mõju Riesi meteoriidikraatri pindmiste süeviiitide muutumisele praktiliselt puudub või ei ole eristatav ning valdav süeviiitide muutumine toimub pindmisel murenemisel.

Pindmiste süeviiitide madala-temperatuurilist päritolu kinnitavad ka smektiidi isotoopkoostise ($\delta^{18}\text{O}$ ja δD) uuringud, mille alusel hinnatud fluidi temperatuurid (eeldades, et smektiit moodustud klaasi ümberkristalliseerumisel tasakaalus süsteemis ringelnud veefluidiga) on 16.0 ± 4.8 °C, mis suhestub hästi kraatri piirkonnas viimase 15 miljoni aasta hinnatud temperatuurivariatsioonidega. Tüüpiliste muremisprotsesside päritolu tõenduseks pindmistes süeviiitides on ka hapniku isotoopide fraktsioneerumise järgi arvatud fluidi $\delta^{18}\text{O}$ väärtused $-6.9 \pm 1.05\%$, mis vastavad nii piirkonna kaasaegsete sademete $\delta^{18}\text{O}$ koostisele -7% , kui ka sademete vee koostisele ($-5.9 \pm 1.7\%$) Kesk-Miotseenis, vahetult peale kraatri moodustumist.

Erinevalt pindmistest süeviiitidest iseloomustavad kraatrit täitvate süeviiitide hüdrotermaalseid muutuseid/ilminguid sekundaarne savimineralisatsioon ja tseoliidistumine, millega kaasneb varajane K-metasomatism koos albitiseerumise ja kloritiseerumise ilmingutega, mis on Osinski (2005) andmetel moodustunud temperatuuridel $\sim 200\text{--}300$ °C. Sellist kontrastset süeviiitide sekundaarset mineralisatsiooni kinnitavad ka Riesi materjali mineraloogilised ning sekundaarsete silikaatmineraalide hapniku ja vesiniku stabiilsete isotoopide uuringud. Nördlingen 1973 puuraugu süeviiitide läbilõikes analüüsitud smektiidi hapnikudeuteeriumi geotermomeetria näitab fluiditemperatuuride gradatasioonilist suurenemist sügavuse suunas ning nendel andmetel ulatusid fluiditemperatuurid kraatrit täitvate süeviiitide alumisel pinnal 150 °C. Tähelepanuväärne on, et need tulemused viitavad $50\text{--}100$ °C madalamale temperatuurile kui seni on hinnatud. Nii Riesi kui ka paljude teiste maailma kraatrite hüdrotermaalsete süsteemide korral on varem oletatud nn ümberpööratud hüdrotermaalset süsteemi, kus muutumistemperatuurid süeviiidi-kompleksi ülemises osas on kõrgemad kui kraatri läbilõike alumistes kihtides. Meie tulemused näitavad seevastu, et smektiidi kristalliseerumisel kasvasid temperatuurid monotoonselt koos sügavusega, mis viitab nõ normaalsele hüdrotermaalse süsteemi geotermaalsele situatsioonile.

Nendest tulemustest lähtudes võib püstitada impakt-indutseeritud hüdrotermaalsete süsteemide kaheastmelise arengumudeli. Impakt hüdrotermide tsirkulatsiooni algaasis, kui sulaklaasi massidest rikastunud süeviiidi temperatuurid ulatuvad >500 °C ning tulenevalt kuumutatud kivimite plastsetest omadustest on konvektiivsete tsirkulatsioonisüsteemide moodustumine takistatud, domineerib impaktkivimite termaalne kontaktmoone ja pneumatolüütiline muutumine, mille termaalne väli võib lähtudes süeviiitide soojusvälja anomaaliast olla nn ümberpööratud asendis. Kivimite jahtumisel allapoole plastse ja hapra deformatsiooni piiri (temperatuurid <400 °C) saab võimalikuks avatud püsilõhedega kivimis fluidide konvektiivne tsirkulatsioon ning kraatris (süvendis) realiseerub nn normaalsete gradiendivektoritega geotermaalne väli, mida registreerivad impakti jahtumise lõppfaasis moodustunud sekundaarsed hüdraatfaasid.

Hüdrotermaalsete fluidide koostiselise evolutsiooni selgitamiseks Riesi kraatris viidi läbi smektiidi faaside boori stabiilsete isotoopide uuring, mille tulemuste interpreteerimiseks koostati boori isotoopvahetuse ja massiülekanne geokeemilised mudelid. Boori stabiilsete isotoopide süsteemi massisõltuvuslik fraktsioneerumine trigonaalselt ja tetragonaalselt koordineeritud boori seisundite vahel on tundlik keskkonna indikaator, mis sõltub temperatuurist, fluidi pHst, soolsusest ja arvatavasti ka mineraalse faasi kristallstruktuuri iseärasusest. Riesi kraatri süeviidide boori isotoop-süsteemi mudeli analüüs näitab, et pindmiste süeviidide muutumine on toimunud madalatemperatuurilises madala pH (5–7) ja ionkontsentratsiooniga (nt sademete vesi) veelises keskkonnas. Seejuures viitab boori (B) ja vesiniku isotoopide seaduspärane varieerumine võimalusele, et sekundaarsed smektiidi mineraalide faasid on omandanud (analoogselt hapniku isotoopsüsteemile) sademete mineraal-vesi isotoopvahetuse fraktsioneerunud koostise. Sellist sõltuvust ei ole varem B isotoopidele leitud. Siiski näitab massiülekanne ja isotoopvahetuse mudel, et juhul kui oletada B isotoopkoostise ülekandumist savifaasi, siis tulenevalt sademete mitu suurusjärku väiksemast B sisaldusest nõuaks see protsess miljoneid aastaid.

Isotoopvahetusmudeli rakendamine kraatrit täitvate süeviidide koostisele näitab, et võrreldes pindmiste süeviididega on nende muutumine toimunud kõrgematemperatuurilises (~100 °C) fluidis, mille pH varieerus >7–8 ning mis võis olla kõrge ionkontsentratsiooniga. Selline fluidikoostis tõendab sisemiste süeviidide muutumisel tekkinud savimineraalide hüdrotermaalset päritolu anioonhüdrolüütiliselt neutraliseeritud ja lahustuvate komponentide suhtes rikastunud fluidist. Siiski ei ole võimalik praeguste tulemuste põhjal selgitada, kas ja millisel määral võis Riesi kraatri hüdrotermaalne süsteem tootuda vahetult peale kraatri tekkimist moodustunud meso-haliinse ja leeliselise-veelise järve veest.

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Impaktkraatrid, planeetide impaktprotsessid, impakt-indutseeritud hüdrotermaalsed süsteemid ning selle mineraloogilised muutused, madala-temperatuuriline geokeemia, stabilised isotoobid.

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