Post-impact alteration of surficial suevites in Ries crater, Germany: Hydrothermal modification or weathering processes?

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Abstract–Alteration of surficial suevites at Ries crater, Germany was studied by means of X-ray diffraction and scanning electron microscopy. Here, we discuss the origin of hydrous silicate (clay) phases in these suevites that have been previously interpreted as resulting from post-impact hydrothermal processes. The results of this study indicate that the dominant alteration phases are dioctahedral Al-Fe montmorillonite and halloysite, which are typical low temperature clay minerals. We suggest that the surficial suevites are not altered by hydrothermal processes and that alteration occurred by low temperature subsurface weathering processes. If the surficial suevites were indeed hydrothermally modified during the early stages of post-impact cooling, then the alteration was of limited character and is completely masked by later weathering.

INTRODUCTION

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 (see Pohl et al. 1977 and Engelhardt 1990, for reviews of the Ries geology and impactites). 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).

Impact-induced hydrothermal activity (IHT) occurs following meteorite impacts in water- or ice-rich targets due to differential temperatures in the impact heated and/or melted crater rocks (see Naumov [2005] for a review). IHT 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, 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). 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 albitionization 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. 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 remains poorly constrained. Similarly, Ames et al. (2004) concluded from mineral assemblages of impactites in core Yaxcopoil-1, Chicxulub impact crater, that the alteration of impact glasses has resulted from low temperature seawater interaction rather than typical high temperature hydrothermal alteration.

In this contribution we study the composition of the secondary phases within surficial 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. Our aim is to determine the origin of these phases—i.e., low-temperature hydrothermal mineralization versus diagenetic devitrification and aerial-to-subaerial weathering of surficial suevites.

IHT ALTERATION ASSEMBLAGES

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. 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. 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 et al. 2005).

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. 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).

GEOLOGICAL SETTING

The Ries impact crater is a 24 km diameter complex impact structure in southern Germany (Pohl et al. 1977) (Fig. 1). The age of the Ries event has been constrained by dating of suevite glasses at 15.1 ± 0.1 Ma using the ⁴⁰Ar/³⁹Ar step-heating method (Staudacher et al. 1982), and more recently, 14.3 ± 0.2 Ma by the ⁴⁰Ar/³⁹Ar laser-probe technique (Buchner et al. 2003).
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 inner 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 inner basin is entirely formed in crystalline basement and filled by crater-fill suevites overlain by ~400 m of post-impact lacustrine sedimentary rocks (Pohl et al. 1977). The outer zone of the structure is overlain by different types of proximal impactites (Engelhardt 1990): (1) Bunte Breccia; (2) polymict crystalline breccias; (3) surficial 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).

Surficial suevites contain components from the crystalline basement at all stages of shock metamorphism and shock-melted glassy inclusions, specifically vitreous and devitrified impact glass (Engelhardt et al. 1995; Engelhardt 1997). Surficial suevites are found in a large number of small isolated patches inside the morphological rim and up to radial distances of ~14 km beyond the rim to the south-southwest and east-northeast (Fig. 1). The thickness of the layer 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). The surficial suevite is lithologically different from the so-called crater-fill suevite, which is only observed in drill cores. The crater-fill suevite forms 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 massive main 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 the 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).

**MATERIAL AND METHODS**

The surficial suevites studied here were collected from 4 outcrops within and around the Ries impact structure (Fig. 1). Altogether 28 samples were studied. Samples include suevites that varies from fresh (with no or limited noticeable alteration) to highly altered. The samples include also wall rocks of degassing pipes from locations at Altenbürg, Aumühle, and Oettingen. In addition, 2 samples of coherent impact melt rock (“red suevite”) were analyzed from Polsingen outcrop. During sampling rock clasts were avoided and only glass rich parts and fine-grained groundmass were handpicked under the binocular for mineralogical and chemical analyses. “Glass shards” are here defined as dark violet-grey glassy inclusions in suevite mass. The surface of glassy particles was cleaned but no attempt was made to separate the glass and crushed rock particles inside the inclusion. “Suevite groundmass” is defined here as a fine-grained mixture of glass and crushed rock particles. A complete list and description of the studied samples is given in Table 1.

The mineralogical composition of samples was studied by means of X-ray powder diffractometry (XRD). The XRD patterns of whole-rock samples were measured in grinded and homogenized unoriented powder samples with DRON-3M diffractometer (University of Tartu) using Ni-filtered Cu-Kα radiation in the 20 range between 2 to 50 or 60°, with a step size of 0.03 or 0.05 °20 and 5 seconds counting time.

Clay minerals were separated by standard sedimentation procedures. The <2 μm size clay fraction was flocculated and
Sr$^{2+}$-saturated with 0.1 M SrCl$_2$. Excess salt was removed by repeated rinsing with distilled water and ethanol. Oriented clay aggregates were made by smearing the clay pastes onto glass slides. XRD data of oriented air-dry and ethylene glycol-solvated (EG) preparations were obtained using a DRON-3M diffractometer with Ni-filtered Cu $K\alpha$ radiation. Scanning steps of 0.03° 2θ from 2 to 30 or 50° 2θ and a counting time of 4 s per step were used for clay slides. The ambient relative humidity varied from 60% to 65%. The Green-Kelly Li-test according to Muravyov (1970) was applied to distinguish the tetrahedrally substituted beidellite and octahedrally substituted montmorillonite.

The XRD patterns were analyzed and modeled by using SIROQUANT-2.5\textsuperscript{TM} (Taylor 1991) for unoriented powders and MLM2C code (Plançon and Drits 2000) for oriented clay aggregates, respectively. 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, accelerating voltage of 25–30 kV, a beam current of 5 nA (University of Tartu). The SEM specimens were coated with gold. The interpretation of the SEM images was checked against the EDS spectra.

### RESULTS

#### XRD—Whole-Rock Mineralogy

The mineralogical composition of the studied whole-rock samples is summarized in Table 2 and representative XRD patterns of unoriented samples are shown in Figs. 2a and 2b. The mineralogical composition of the suevites is characterized by an assemblage of montmorillonite-type smectite, plagioclase, quartz, and K-feldspar. Both the qualitative and quantitative composition of different suevite types is rather persistent and does not show any variation between different locations. However, highly altered suevites, particularly those at Lehberg were found to contain halloysite, in remarkable amounts (up to 81 wt% of crystalline phases).

#### Smectite

The most prevalent mineral phase in the suevites is smectite, which is evidently a dioctahedral montmorillonite phase (Fig. 2c). The average content of montmorillonite is ~34 wt%, but its content can vary from 4.8 to 64 wt% (Table 2). In the groundmass of fresh-suevites, the content of montmorillonite ranges from 23 to 45 wt%. Its abundance in
Table 2. Mineralogical composition of bulk suevite in wt%, based on XRD analyses. The estimated standard deviations of the weight percentages are shown in brackets, tr—trace amount (<0.5 wt%).

<table>
<thead>
<tr>
<th>Lab no.</th>
<th>Location</th>
<th>Quartz</th>
<th>Coesite</th>
<th>K-feldspar</th>
<th>Plagioclase</th>
<th>Smeectite</th>
<th>Halloysite</th>
<th>Calcite</th>
<th>Dolomite</th>
<th>Hematite</th>
<th>Zeolite</th>
<th>Amphibole</th>
<th>Garnet</th>
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<tr>
<td>RS1-1</td>
<td>Aumühle</td>
<td>15.3 (0.21)</td>
<td>2.1 (0.17)</td>
<td>11.8 (0.82)</td>
<td>32.1 (0.50)</td>
<td>34.9 (0.52)</td>
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<td>1.8 (0.15)</td>
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<td>Aumühle</td>
<td>16.8 (0.47)</td>
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<td>22.7 (0.52)</td>
<td>44.1 (0.63)</td>
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<td>10.5 (0.26)</td>
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<td>33.4 (0.81)</td>
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<td>17.7 (0.04)</td>
<td>3.0 (0.20)</td>
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<td>41.2 (0.62)</td>
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<td>25.2 (0.73)</td>
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<td>12.1 (2.07)</td>
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<td>37.3 (1.33)</td>
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<td>7.6 (0.28)</td>
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<td>33.4 (0.72)</td>
<td>43.1 (0.73)</td>
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<td>28.1 (0.51)</td>
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<td>8.7 (1.18)</td>
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<td>Lehberg</td>
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<td>2.4 (0.21)</td>
<td>3.3 (0.32)</td>
<td>15.7 (0.45)</td>
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<td>24.0 (0.46)</td>
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<td>11.8 (1.23)</td>
<td>16.5 (0.42)</td>
<td>56.6 (0.73)</td>
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<td>44.9 (0.67)</td>
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<td>4.8 (0.44)</td>
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<td>Oettingen</td>
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<td>4.3 (0.66)</td>
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<td>Oettingen</td>
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<td>2.5 (0.30)</td>
<td>4.0 (0.55)</td>
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the glass rich surficial suevite groundmass is about the same varying from 10 to 44 wt%, but these samples show on XRD patterns also a remarkable bulge of amorphous maximum (see Fig. 2d) indicating the presence of still a large amount of vitrous glass in the groundmass. Highly altered suevites show a somewhat higher smectite content (18.8–59 wt%), except in sample of a suevitic dike where the smectite content was significantly lower, i.e., 4.8 wt%.

**Plagioclase**

The groundmass of the suevite and impact glasses of Ries surficial suevites is characterized by the presence of plagioclase. Structural refinement of the XRD data indicate that the plagioclase is oligoclase-andesine with 25–45 mol% anorthite (An) component in good agreement with microprobe data for plagioclase in Ries suevites (Engelhardt 1997; Osinski 2004). The large XRD reflection widths indicate that the plagioclase is evidently structurally disordered and/or poorly crystallized with extremely small coherent stacking domain sizes. The highest content of plagioclase was found in isolated glass shards from the suevite, where it composes up to 67 wt% of crystalline mineral matter. The lowest amounts of plagioclase are found in the highly altered suevites, where its content is on average less than 24 wt%.

**Quartz**

The quartz content of the studied samples is rather constant, with an average of 14 wt%. There are no significant differences in quartz content between the groundmass and the glass clasts in suevite. The content of microcristalline quartz varies from 12 to 19 wt% in the groundmass, and from 11 to 25 wt% in the glass phases. In the highly altered suevite the amount of quartz is about 14 wt% or slightly less, except in sample RS 16-2 of a suevitic dike with a quartz content of up to 34 wt%. A variation in the quartz content occurs in degassing pipes at interior surfaces of pipes rich in calcite, the quartz content ranges from 3.6 wt% to 11 wt%, whereas in wall rock of the pipes the quartz content was as high as 28 wt%.

Coesite, a high-pressure polymorph of quartz was identified in several suevite samples (Fig. 3a). The highest coesite content (8 wt%) was found in a fresh glass of a suevite from the Aumühle location. In most cases, coesite occurs only in trace amounts (<2 wt%). In addition, in highly altered suevites, opal-CT and alpha-cristobalite phases may be present, yet quantification by XRD is limited due to their poorly crystallized nature.

**K-Feldspar**

XRD analysis indicates variable amounts of K-feldspar in all samples, ranging from trace amounts up to an exceptional 61 wt% in sample RS17-1, a “red suevite.” Though, the highest values are found in impact melt rocks (samples RS17-1, RS17-2 and RS7). There the K-feldspar is a high-temperature sanidine in keeping with the melt rock interpretation of red suevites by Osinski (2004). The average value of K-feldspar in suevitic samples is about 7 wt%.
Halloysite

Halloysite is a kaolinite group mineral and originate by intensive alteration (leaching) of aluminosilicate minerals, such as feldspars (Meunier 2005). In the Ries samples, halloysite occurs in the highly altered suevites, particularly those from Lehberg. In the groundmass of highly altered suevite samples the content of halloysite is <4 wt%, except for sample RS5-1 with a halloysite content in groundmass of up to 14 wt%. The halloysite content is remarkably high in altered gneiss fragments within the highly altered suevites ranging from 17 up to 81 wt%. Halloysite is recognized in two structural forms: (i) 10 Å halloysite, and (ii) 7 Å halloysite (Fig. 3b). Traces of halloysite have been identified also in other samples, but its content is generally less than 2 wt%.

Calcite

Calcite was recognized in samples of surficial suevites from Aumühle, Altenberg and Lehberg, comprising <2–4 wt%. The highest calcite content was found in degassing pipes at the Altenbürg quarry, reaching peaks in samples RS10 and RS11 75 wt% and 32 wt%, respectively.

Minor Phases

The content of other mineral phases in the Ries samples was usually less than 3%. Typically, trace amounts of pyroxene, amphibole, hematite, and garnet were identified. Amphibole and pyroxene were recognized in samples RS9 and RS20, with contents of 1.4 and 6.2 wt%, respectively. The amount of hematite ranges from 2.3 to 3.8 wt% in samples RS12 and RS7, respectively. Garnet (andradite) was identified in few samples in small amounts, <2 wt%.

Zeolites have been recognized in the groundmass and impact glass clasts of surficial suevites by several authors (e.g., Engelhardt and Graup 1984; Osinski et al. 2004; Osinski 2005). In this study only harmotome was recognized in one Altenbürg sample (degassing pipe) with amounts of ∼2.7 wt%. Osinski (2005) recognized various zeolite minerals at six locations; however, none of these sites were studied here.

XRD—Clay Mineralogy

The clay fraction of the suevites (<2 µm) is characterized by montmorillonite-type smectite as indicated by strong 001 reflection at 14–15 Å-s in air-dry state that expands to 17 Å in ethylene-glycolated state (Figs. 3c,d). In some samples, halloysite along with smectite was identified. Halloysite was found in the same samples where it was identified in whole-rock XRD analysis.

The smectite nature of the clays was confirmed by applying the Green-Kelly Li-test (Murayov 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. Structure refinement indicates that the montmorillonite is of Al-Fe 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., Haymon and Kastner 1986; Meunier 2005).

The structural composition of smectite does not show any variance regardless of 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 been induced by temperature gradients.

Scanning Electron Microscopy

The SEM study was undertaken to study the occurrence and spatial distribution of clay minerals as a major secondary phase. SEM images illustrating characteristic morphologies and distinctive textures of minerals or rock of the Ries suevites are shown in Figs. 4 and 5.

Freshly broken interior surfaces of a suevite sample show the typical vesicular structure of groundmass and melt phases. The glass phase has frequently a flow-texture (Fig. 4a) and contains irregularly shaped vesicles. All samples show the ubiquitous clay coatings and vesicles within the glasses are lined by clay aggregates (Fig. 5), which is consistent with the high percentage of clay in the suevite identified by XRD analysis. In addition, other authigenic minerals such as calcite, plagioclase(?), halloysite(?) and opal-CT were identified by EDS spectra and characteristic morphology replacing the vitric matrix and glass fragments in studied suevites.

Petrographic relations indicate that smectite was the first and the major mineral to form. The lepispheres of opal-CT that rarely coexist with smectite (Fig. 4) appear to postdate the major smectite formation. The initial devitrification of glasses proceeds most probably by slow dissolution indicated by micrometer scale dissolution pits on the glass surfaces in fresh suevites. These etched surfaces are apparently related to glass dissolution (Figs. 4c and 4d).

The SEM images indicate that the smectite precipitation is initiated at the glass surfaces in two different arrangements — as spherical aggregates of sub-radial orientation of smectite crystallites and as flaky smectite crystallite aggregates that form loose pseudo-polygonal webs known also as “honey comb” or “corn-flake” microstructures (Meunier 2005) on the fresh glass surface (Fig. 5). 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). Halloysite was identified in highly altered suevite samples either as delicate vermiform dendritic aggregates growing into the vesicular cavities and pore space or massive aggregates of dendritic crystallites filling the space between glass vesicle polymorphs of smectite aggregates (Fig. 6).

DISCUSSION

Hydrothermal Alteration versus Weathering

Smectite with a composition corresponding to dioctahedral Al-Fe montmorillonite is the principal product of alteration in the surficial suevites of Ries crater. Its composition and structural state does not show any significant variation between the different sampling localities at the Ries crater. This finding is not consistent with a hydrothermal origin of the suevite clay by post impact “alteration”. Hydrothermal alteration in active endogenic 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 °C km⁻¹ occurs within the hottest central parts of an impact structure (Masaitis and Naumov 1993; Naumov 2005; 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. This general understanding fully agrees with the alteration to clay mineral observed in surficial suevites at Ries crater. The dominant smectitic alteration of these suevites with halloysite in highly altered suevites is best explained by a low temperature hydrous devitrification of the impact glasses and not by hydrothermal alteration.

Alteration of Ries suevites has been noted since the early 1970s (e.g., Engelhardt 1972; Chao et al. 1978; Newsom
et al. 1986; Osinski 2005). Indeed, the IHT 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. All impact glasses in the crater-fill suevite are completely replaced by various secondary minerals (Stöffler et al. 1977). In these rocks argillic alteration (predominantly montmorillonite, saponite, and illite) and zeolitization (predominantly analcime, erionite, and clinoptilolite) can be observed (Pfannschmidt 1985; Osinski 2005). There is an additional early phase of K-metasomatism accompanied by minor albitionization and chloritization at temperatures of approximately 200–300 °C. 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 IHT alteration within surficial suevites is typically restricted to smectite with a composition corresponding to dioctahedral Al-Fe montmorillonite with minor zeolite (mainly phillipsite) deposition within cavities and fractures (cf. Newsom et al. 1986; Osinski et al. 2004; Osinski 2005). It has been generally accepted that these clays formed by post-impact hydrothermal alteration of impact-generated glasses and/or finely comminuted crystalline basement material (Engelhardt 1972; Stähle 1972; Engelhardt and Graup 1984;
Fig. 5. Micrographs (SE images) of smectite “corn-flake” aggregates. A—initial globular/spheroidal aggregates on the glass surface; B—cross section of a layer of box-work smectite aggregates on the glass surface; C, D, E, F—smectite aggregates lining the inner surfaces of vesicles.
Newsom et al. (1986, 1990). The same was assumed for the origin of calcite in the Ries surficial suevites. However, recent studies have suggested that calcite and a substantial proportion of the fine-grained “clays” in the groundmass of surficial suevites represent a combination of primary impact-generated melt phases and high temperature devitrification products (Graup 1999; Osinski 2003, 2005; Osinski et al. 2004), which are altered to smectite type clays on various scales. As a result, secondary hydrothermal alteration of the surficial suevites is definitely less important than previously thought, if it occurred at all.

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. Newsom et al. (1986) previously noted that the lack of illite-smectite type mixed-layering in the montmorillonite constrains the main alteration event in this unit to temperatures <100–130°C. It is noteworthy that similar secondary calcite and montmorillonite precipitation also occurs within cavities and fractures in the all types of the proximal impactites—Bunte Breccia, polymict crystalline breccia—that were not heated enough or cooled too rapidly for IHT initiation. Alternatively, Kieffer and Simonds (1980) predicted the formation of clays by penecontemporaneous alteration of ejecta by hot volatiles during the actual formation of the crater. Similarly, it has been suggested that during bentonite formation, the volcanic glass is altered very early in the volcanic context and sedimentation of bentonite involves already transformed ash, or the alteration may take place during ash fall (e.g., Grim 1968). However, this kind of transformation is considered to date as improbable (Meunier 2005) and we consider this type of alteration as irrelevant for the Ries surficial suevites.

Engelhardt (1972) noted that pipe like structures (“vertical chimneys”), which intersect the suevite in several suevite outcrops, indicate the degassing of the breccia. Chao et al. (1978) described these as pathways for hydrothermal fluids and as the sites of intense alteration. He suggested that the interior surfaces of the degassing pipes are coated with (hydrothermal) clays. Newsom et al. (1986) studied the degassing pipes in detail and found that the surfaces of degassing pipes are not coated with clay minerals, but a thin (<2 µm) layer of iron oxide or hydroxide. They suggested that the absence of clay in the pipes indicates that 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. Moreover, 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.

**Smectite Formation**

Smectite is one of the major alteration products of volcanic glass (e.g., Tomita et al. 1993; Fuente et al. 2002) and it is recognized as an important secondary phase in impact glasses (e.g., Naumov 2005). Usually, the formation of smectite from a siliceous glass proceeds through removal of excess of Si and alkali compounds. As the consequence the smectite is a typical alteration product in open to half-open
systems. However, if sufficient Si and alkalis are retained in
half-open or nearly closed systems then zeolites and/or
authigenic quartz polymorphs (opal, cristobalite) form.

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 (see Fig. 4). Randomly oriented montmorillonite-type
smectite flakes fill or coat the walls of existing round cavities
and pores 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. One question
that arises is why not all the glasses have been transformed.
Phases that are now clay are seen to be intimately intergrown
with unaltered silicate glasses (e.g., see Fig. 8 in Osinski et al.
2004). One possible explanation is that the unstable hydrous
impact melt glasses were transformed into clays, leaving the
more stable volatile-free impact glasses fresh.

In addition to smectite, alteration of the suevite glass was
accompanied by formation of minor halloysite. Both secondary
phases appear to have formed broadly contemporaneously
from the glass, although the halloysite is found in the most
heavily altered suevites and is likely a later alteration phase as
denoted by the most intensively weathered rocks as at the
Lehberg locality. There, most fractured, and therefore, well
permeable monomict (gneiss) breccias are host rocks to
suevite dykes. The brecciated nature of these gneisses has
allowed strong leaching of suevite dykes by percolating
surface waters. The formation of halloysite at conditions
generally promoting the conversion of glass to smectite is
interpreted to result from more intense percolation of slightly
acidic meteoritic waters through highly porous suevites. 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 IHT fluids, however, depends upon the composition of the
target rocks (e.g., crystalline versus sedimentary, maffic
versus acidic rocks) present at the impact site as well as on the
fluid source. IHT fluids are typically weakly alkaline to near
neutral and supersaturated in silica during the entire
hydrothermal process (Naumov 2005).

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 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.
Indeed, most of the earlier zeolite findings are reported in more
fine-grained suevites outside of crater rim (e.g., Osinski 2005),
which probably were characterized by lower hydraulic
conductivity and could have provided sufficiently high Al/Si
saturation of pore water for zeolite precipitation. However,
cristobalite and opal-CT, which were identified in some suevite
samples from crater interior, indicate that an excess of silica
was probably present in the solution and at least opal-CT
formed paragenetically later than smectite.

CONCLUSIONS

The mineral composition of altered surficial suevites at
the Ries impact crater shows that the dominant alteration
phase is smectite with a composition corresponding to
dioctahedral Al-Fe montmorillonite. This is a typical low
temperature smectite pointing to weathering as the major
reason for alteration without evidence of hydrothermal
modification. According to microscopic evidence the impact
glasses have been transformed directly to smectite through
dissolution-precipitation mechanisms without intermediate
amorphous precursor and/or primitive clay masses.

The low temperature hydrous devitrification of the
impact glasses is verified by the occurrence of halloysite in
highly altered suevites. The composition and the structural
state of the clay phases do not show any significant variation
within the structure. 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.

These results indicate that the surficial suevites are not
altered by hydrothermal processes as suggested earlier and
that the alteration has occurred due to low temperature
subsurface weathering processes. If the surficial suevites
were indeed hydrothermally modified at the early stages of
cooling after the cratering event, then the alteration was at a
limited scale and is now completely masked by later
weathering. This is consistent with the suevites themselves
being the main heat source for an impact-induced
hydrothermal system at the Ries crater; therefore, impact-
induced hydrothermal activity has only played a role in the
References


