

## HISINGERITE MATERIAL FROM A BASALT QUARRY NEAR GEELONG, VICTORIA, AUSTRALIA

AHMAD SHAYAN

CSIRO Division of Building Research, P.O. Box 56, Highett, Victoria 3190, Australia

**Abstract**—A material resembling what has been described in the literature as hisingerite has been identified in the joints of Cenozoic grey basalt near Geelong, Victoria. The material gives an X-ray powder diffraction pattern with weak broad peaks at 4.49, 2.58, and 1.53 Å and a chemical analysis of  $\text{SiO}_2 = 34.2$ ,  $\text{TiO}_2 = 0.28$ ,  $\text{Al}_2\text{O}_3 = 4.16$ ,  $\text{Fe}_2\text{O}_3 = 17.10$ ,  $\text{FeO} = 3.52$ ,  $\text{MnO} = 0.04$ ,  $\text{MgO} = 5.19$ ,  $\text{CaO} = 0.68$ ,  $\text{Na}_2\text{O} = 0.26$ ,  $\text{P}_2\text{O}_5 = 0.05$ ,  $\text{H}_2\text{O}^+ = 5.3$ ,  $\text{H}_2\text{O}^- = 25.4$ , total = 96.18% (3.82% siderite impurity). Assuming a smectite model with 44 negative charges per unit cell, the chemical composition gives a unit-cell formula with -1.14 charges, corresponding to a cation-exchange capacity (CEC) of 135 meq/100 g. The same unit-cell charge is obtained when the structural formula is calculated on the basis of  $(\text{Si} + \text{Al}) = 8$ . The measured CEC of 60 meq/100 g indicates that the smectite structure may not apply to this hisingerite-material, and that in the alternative structure, all of the Al atoms may not be in the tetrahedral positions. Although the specific surface area of this material is between 662 and 758  $\text{m}^2/\text{g}$  (comparable to that of smectite), the infrared spectra do not show the characteristic OH vibrations, and the thermal analysis curves lack the dehydroxylation peak at 550–600°C expected for a smectite. Transmission electron microscopy shows indications of a layer structure and apparently hollow spherical bodies with ‘onion’ structure of 140 to 200 Å internal diameter, which might represent the sites of the large amounts of water contained by the material. The mode of occurrence and the nature of the hisingerite-material suggest precipitation from solution at relatively low temperatures.

**Key Words**—Electron diffraction, Hisingerite, Infrared spectroscopy, Iron, Saponite, Transmission electron microscopy.

### INTRODUCTION

Materials referred to in the literature as hisingerite are poorly ordered, hydrous iron silicates with variable compositions which occur in a variety of geological environments, e.g., with sulphide ore bodies, with siderite, as an alteration product of ferromagnesian silicates, and as a result of the weathering of Fe-rich saponite (see Brigatti, 1982). The mineralogical nature of these materials is rather controversial. In earlier studies, based on X-ray powder diffraction (XRD) and chemical analysis, “hisingerite” was considered to be amorphous or cryptocrystalline (Gruner, 1935; Sudo and Nakamura, 1952; Bowie, 1955), with weak, broad XRD lines corresponding to the intense lines of nontronite, but without a major line at 12 to 14 Å. Whelan and Goldich (1961) and Lindqvist and Jansson (1962), respectively, suggested a saponite and a mica structure for “hisingerite.” Kohyama and Sudo (1975) showed that “hisingerite” crystallites were variable in composition, falling between trioctahedral iron-rich saponite and dioctahedral nontronite. Wada (1982), classifying Fe-bearing amorphous clay minerals according to  $\text{SiO}_2/\text{Fe}_2\text{O}_3$  ratio, recognized an Fe-rich “hisingerite” that had a poorly ordered and finely crystalline 2:1 layer silicate structure, and he also regarded as “hisingerite” Si-bearing ferrihydrites with  $\text{SiO}_2/\text{Fe}_2\text{O}_3$  ratios lower than 0.5.

Brigatti (1982) recalculated the composition of many “hisingerites,” nontronites, saponites, and Fe-rich

montmorillonite on the basis of a common formula (smectite), and applied a multivariate analysis to these formulae to establish the range in composition of “hisingerite” and to characterize it in relation to these minerals. She concluded that “hisingerite” was a well-defined trioctahedral mineral and could be grouped with the Fe-rich smectites. Clark *et al.* (1978), however, did not support a layer-structure for “hisingerite” and considered such materials to be iron-rich members ( $\text{Fe} > \text{Mn}$ ) of the solid solution series between  $\text{MnSiO}_3 \cdot \text{H}_2\text{O}$  (neotocite) to  $\text{FeSiO}_3 \cdot \text{H}_2\text{O}$  (hisingerite), which were concluded to be gel-like or very poorly crystalline. Eggleton *et al.* (1983), using more powerful techniques such as transmission electron microscopy, X-ray radial distribution function analysis, X-ray absorption edge spectroscopy, Mössbauer spectroscopy, and chemical analysis, also concluded that their neotocite and “hisingerites” were noncrystalline or gel-like materials. Their “hisingerites” consisted of hollow spheres of 50–100 Å diameter with a rudimentary structure, possibly Si-rich, and (Fe,Mn)-rich layers, in the outer 10–20 Å of the spheres. Considering the large variation in the chemical compositions and origins of the “hisingerites” reported in the literature, it is possible that some differences exist in their nature so far as the degree of crystallinity and structure is concerned.

In Australia, hisingerite was reported among the gangue minerals of a Broken Hill mine (Eggleton *et al.*, 1983), associated with sulphide minerals of a mine at

Cobar, New South Wales (Slansky, Geological Survey of New South Wales, Sydney, personal communication, 1982), and in a gold mine in Western Australia (Schwartz, 1924). The present paper describes the occurrence and chemical and mineralogical properties of hisingerite-material found in a basalt quarry near Geelong, Victoria.

### OCCURRENCE

The basalt quarry is located at Fyansford, a western suburb of Geelong, on an ancient river gully filled with the extensive Cenozoic 'Newer Volcanics.' An upper, partly weathered grey basalt is underlain by an altered black basalt with a high smectite content (~40%). A third flow consists of two layers: an upper grey basalt showing only minor alteration of glass to palagonite, grading into a lower greenish basalt with deuteric alteration of glass and olivine to chlorite/smectite minerals.

The hisingerite material occurs in crusts, about 2–15 mm thick, on cooling joints and fracture planes of the lowermost grey basalt. Although some thin crusts are homogeneous, thicker pockets of hisingerite are surrounded by massive siderite or include sub-parallel layers of paper-thin siderite. The hisingerite material is black with a vitreous luster and conchoidal fracture and yields a greenish-grey powder. Thin (1 mm) fragments are brown in reflected light.

### EXPERIMENTAL

Thin sections were made for petrological examination of the grey basalt and the hisingerite material. Optically pure fragments, having a vitreous luster, were hand picked and ground to <75  $\mu\text{m}$ . Suspensions with a solid to solution ratio of 1:20, made with distilled water or a 0.01 M  $\text{CaCl}_2$  solution, were used for pH measurement. Exchangeable cations were measured by atomic absorption spectrophotometry on extracts made with neutral 1 M ammonium acetate. The specific surface area was measured using the ethylene glycolmonoethyl ether (EGME) retention method of Eltantawy and Arnold (1973). Total elemental analysis was carried out by the Australian Mineral Development Laboratories using a combination of inductively coupled plasma-atomic emission spectroscopy and chemical methods. XRD patterns were obtained for powder samples, using a Philips diffractometer and monochromatic  $\text{CuK}\alpha$  radiation. Infrared (IR) spectra were run on a Perkin Elmer 1430 ratio-recording instrument using 0.5-mg samples in 200-mg KBr disks. Differential thermal (DTA) and thermogravimetric (TGA) analyses were made simultaneously on a Stanton Redcroft ST781 thermal analyzer using 20-mg samples and a heating rate of 10°C/min. A JEOL 100 CX instrument was used for transmission electron microscopy (TEM) and electron diffraction analysis.

Table 1. Exchangeable and soluble cations of hisingerite material, Geelong, Australia.<sup>1</sup>

Extractant	Na	K	Ca	Mg	$\Sigma$ cations
$\text{NH}_4\text{OAC}$	10.2	1.13	0.53	56.7	68.6
$\text{H}_2\text{O}$	8.1	0.33	0.18	1.93	10.5

<sup>1</sup> meq/100 g extracted by neutral 1 M  $\text{NH}_4\text{OAC}$  and water, respectively.

### RESULTS

#### Petrology

The grey basalt is finely vesicular and consists of olivine phenocrysts, an ophitic matrix of labradorite laths and augite, and dark glass containing magnetite needles. Orange-brown siderite lines the walls of some vesicles. One specimen of particularly glassy and vesicular lava was covered by a thick crust (10–12 mm) of hisingerite material consisting of golden yellow and isotropic homogeneous pockets of "hisingerite" embedded in a more brownish, mottled mixture of "hisingerite," siderite, and very small amounts of pyrite. Some thinner crusts of the hisingerite material (~2 mm) also contained some siderite and pyrite; others consisted of pure homogeneous "hisingerite" layers, several millimeters thick, among alternate bands of paper-thin siderite (~0.05 mm).

#### X-ray powder diffraction analysis

XRD analysis showed that the earthy, dull, greenish-tinged samples of the hisingerite material contained either pyrite alone or, less commonly, both pyrite and siderite impurities. Dull, black samples, contained mainly feldspar impurity with minor amounts of pyrite. Only the lustrous, black hisingerite-material was free of X-ray-detectable impurities. This material yielded very broad, weak XRD lines at 4.49, 2.58, and 1.53  $\text{\AA}$ , with very strong scattering at low angles (1–4°2 $\theta$ ). This pattern is similar to those of the previously documented "hisingerites" (e.g., Sudo and Nakamura, 1952; Whelan and Goldich, 1961; Linqvist and Jansson, 1962). Saturation of the material with various cations and glycerol treatment did not change the pattern, although heating to 200°C reduced the scattering at low angles. This sample was used in subsequent work.

#### Chemistry

The pH of suspensions of the hisingerite material was 8.40 in water and 7.75 in 0.01 M  $\text{CaCl}_2$ , suggesting the presence of negatively charged surfaces. This possibility was confirmed by the complete adsorption of 3.4 mg of methylene blue dye (organic cation) by 1 g of the hisingerite material in a 4% aqueous suspension. The large amount of exchangeable cations (Table 1)

Table 2. Chemical analysis and recalculated composition<sup>1</sup> of hisingerite material from Geelong, Australia.

	Wt. %	Atoms	Atom occupancy	Charge unbalance
SiO <sub>2</sub>	34.20	Si 6.985	} 8	} -1.015
TiO <sub>2</sub>	0.28	Al 1.00		
Al <sub>2</sub> O <sub>3</sub>	4.16	Fe <sup>3+</sup> 0.015		
Fe <sub>2</sub> O <sub>3</sub>	17.10			
FeO	4.15 (3.52) <sup>2</sup>	Ti 0.04	} 4.59	} -0.122
MnO	0.08 (0.04) <sup>2</sup>	Fe <sup>3+</sup> 2.61		
MgO	5.70 (5.19) <sup>2</sup>	Fe <sup>2+</sup> 0.60		
CaO	0.91 (0.68) <sup>2</sup>	Mn 0.007		
Na <sub>2</sub> O	0.67	Mg 1.33		
K <sub>2</sub> O	0.26		total negative charge = -1.137	
P <sub>2</sub> O <sub>5</sub>	0.05	Mg 0.25	} 0.74	} cation charge = +1.135
H <sub>2</sub> O+	5.30	Ca 0.15		
H <sub>2</sub> O-	25.40	Na 0.27		
CO <sub>2</sub>	1.23	K 0.07		
Total	99.49			

<sup>1</sup> On the basis of 44 negative charges.

<sup>2</sup> Values inside parentheses are those corrected for siderite contamination and used in the recalculated formula.

indicates highly negatively-charged surfaces. The specific surface area of the material was 758 m<sup>2</sup>/g, however, some of the adsorbed EGME was lost after several 1-hour evacuation and equilibration periods, and the measured surface area was reduced to 662 m<sup>2</sup>/g.

The chemical analysis of the hisingerite material (Table 2) shows it to be highly hydrous, like that reported from Japan (Sudo and Nakamura, 1952), both samples being much more hydrous than other reported "hisingerites" (Brigatti, 1982). The Geelong sample is much poorer in Fe<sub>2</sub>O<sub>3</sub> (17.10%) but richer in MgO than most of the reported "hisingerites." Some carbonate is present (CO<sub>2</sub> = 1.23%). Electron probe analysis of the thin siderite layers associated with the hisingerite gave a composition of MgO = 18.66; CaO = 8.50; FeO = 23.43; MnO = 1.35, corresponding to a CO<sub>2</sub> content of 45.67%. The contribution of this impurity to the

analysis of the hisingerite material was calculated on the basis of 1.23% CO<sub>2</sub>, and the corrected values are shown in Table 2.

#### Differential thermal and infrared analyses

The combined DTA and TGA curves (Figure 1) show a large endothermic peak at 95°C associated with a large weight loss, in agreement with the water content listed in the chemical analysis. An additional weight loss took place gradually up to 1000°C, indicating a less accessible, or a more tightly bound, form of water. The two small exothermic peaks between 412° and 460°C are probably due to the oxidation of very small amounts of pyrite. No sharp dehydroxylation process was evident from the thermal curves, indicating that the structure does not contain OH groups with a uniform bonding to the cations, such as that present in the octahedral layer of smectites.

The IR spectrum of the hisingerite material (Figure 2) is in agreement with the spectra reported for five other "hisingerites" by Whelan and Goldich (1961) and the data given by Van der Marel and Beutelspacher (1976). The bands at 1635, 1660, and 3430 cm<sup>-1</sup> and the shoulder at 3200–3320 cm<sup>-1</sup> are due to the stretching and bending vibrations of water molecules held with different energies. Except for a slight shoulder at 3550 cm<sup>-1</sup>, a well-defined band due to Si–O–H or Fe–O–H vibrations, normally observed for a smectite or hydrous iron oxide, is absent.

#### Transmission electron microscopy

The transmission electron micrograph of the hisingerite-material (Figure 3) shows spherical bodies, very different from the flat sheets commonly observed in

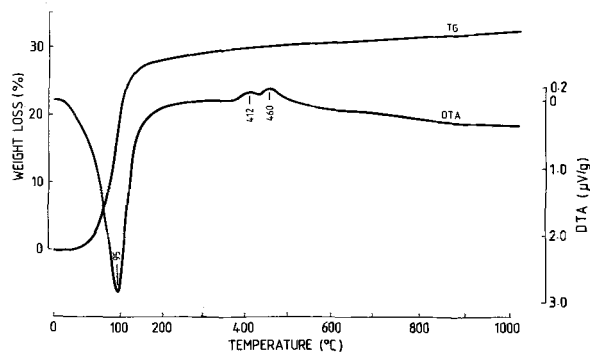


Figure 1. Differential thermal and thermal gravimetric analysis curves of the Geelong hisingerite material showing a large water loss at 95°C, and pyrite impurity indicated by the exothermic peaks at 412° and 460°C.

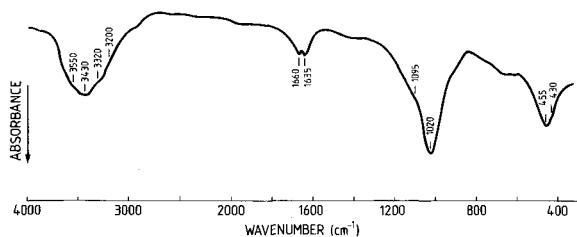


Figure 2. Infrared spectrum of the Geelong hisingerite material showing bending vibrations due to Si–O–Si at 1020  $\text{cm}^{-1}$  and other absorption bands due to water molecules.

samples of saponite and nontronite. At a higher magnification (Figure 4) an irregular arrangement of crystallites and spherical onion structures with internal diameters ranging from 140 to 200 Å are revealed. The outermost layers of some spheres appear to be exfoliating. These spheres may be hollow, holding some water (Eggleton and Keller, 1982) and be responsible for the very large water content of the hisingerite. The lattice image of these materials shows that they are structured, and a  $\sim 4.7$ -Å spacing can be measured between planes perpendicular to the sphere surface (Figure 4), probably corresponding to the 4.49-Å spacing (02 reflections) obtained in the XRD pattern. With a different orientation, a spacing of about 4.5 Å can also be resolved between two plates of the isolated particles on the lower part of Figure 4. Such material is abundant in the upper part of Figure 4 and could have resulted from the exfoliation of spherical bodies. The material is curved and shows a largely random arrangement. Occasion-

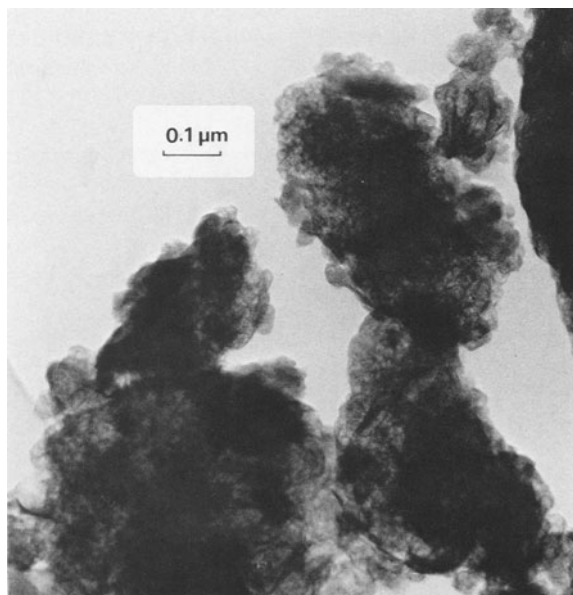


Figure 3. Transmission electron micrograph of the Geelong hisingerite material showing spherical structures.



Figure 4. High resolution image showing structure in the long thread-like material with a spacing of 4.7 Å.

ally, where there is an almost parallel arrangement, spacings of about 9, 11, and 13.6 Å can be measured.

This structure is much more developed than that shown by Eggleton *et al.* (1983) for the Broken Hill "hisingerites." They suggested that such features could be the onset of a layer structure. In the Geelong hisingerite-material the layers would be Si-rich and (Fe,Mg)-rich. The lack of basal reflections, and the broad lines in the XRD pattern of the Geelong material may arise from a poor stacking and small size of the crystallites, and the strong scattering at low angles of the pattern may have been caused by the size and shape of the spherical bodies. Electron diffraction patterns of the material gave spacings at 4.54, 2.64, 2.20, 1.74 and 1.53 Å which fit the  $hk0$  reflections of saponite and are similar to those reported by Lindqvist and Jansson (1962).

## DISCUSSION

The data obtained on the hisingerite-material from Geelong may be interpreted in relation to the possible structures proposed for "hisingerite." Following Brigatti (1982), the structural formula of the hisingerite-material on the basis of a 2:1 layer silicate structure with 44 negative charges per unit cell is shown in Table 2. From the known amounts of exchangeable Mg (Ta-

ble 1) the total number of Mg atoms was separated into exchangeable Mg and that in the structural positions. This structural formula shows incomplete occupation of the octahedral positions (4.59 out of 6), a feature shown also by all of the "hisingerites" reviewed by Brigatti (1982). Her plot of the total number of octahedral Fe atoms vs. the number of octahedral Mg, places nontronites, saponites, Fe-rich montmorillonites, and "hisingerites" in different positions on that diagram. Although statistical analysis of the chemical data led Brigatti (1982) to conclude that "hisingerite" was a definite trioctahedral clay mineral, she did not provide proof of a 2:1 layer structure, on which basis the structural formula was initially calculated. The IR spectra, and DTA and TGA curves of the hisingerite-material from Geelong show that no structural hydroxyl ions are present such as that in the octahedral layer of smectites. Although TEM shows some structure in the crystallites of the Geelong material, which could be interpreted as Si-rich and (Mg,Fe)-rich layers (Eggleton *et al.*, 1983), these layers do not contain hydroxyl ions and are not arranged in the same way as in smectites. The pronounced lattice image of smectites commonly observed by high resolution TEM was not seen for the Geelong material. Therefore, a smectite-like structure cannot be supported for this material.

Eggleton *et al.* (1983) suggested a gel-like structure with a chemical formula of  $(\text{Fe,Mn})_{0.85}\text{SiO}_{3.25} \cdot 2\text{H}_2\text{O}$  for the Broken Hill minerals of the hisingerite-neotocite series, consisting of a framework of  $\text{SiO}_4$  tetrahedra and  $(\text{Fe,Mn})\text{O}_6$  octahedra and forming hollow spheres with about 10% interconnected pore space. Their "hisingerites" are much less developed structurally, as shown by TEM, and are much poorer in  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}$ , and  $\text{MgO}$  and much richer in  $\text{Fe}_2\text{O}_3$  and  $\text{MnO}$  than the Geelong material. The structural formula of the Geelong hisingerite material, based on  $\text{Si} = 8$  (Eggleton *et al.*, 1983), gives  $(\Sigma\text{R})_{0.91}\text{SiO}_{3.15} \cdot 3\text{H}_2\text{O}$  where  $(\Sigma\text{R})_{0.91} = \frac{1}{8}(\text{Ti}_{0.05}\text{Al}_{1.15}\text{Fe}^{3+}_{3.00}\text{Fe}^{2+}_{0.69}\text{Mn}_{0.01}\text{Mg}_{1.81}\text{Ca}_{0.17}\text{Na}_{0.30}\text{K}_{0.08})$ . The Ca, Na, K, and 0.25 of the 1.81 Mg cations are exchangeable rather than structural.

Eggleton *et al.* (1983) did not provide information on the cation-exchange properties of their materials. The above formula does not allow for net negative charges to correspond to the sum of the measured exchangeable cations (60 meq/100 g). Assuming that Al substitutes for Si in the tetrahedral positions, i.e.,  $(\text{Si} + \text{Al}) = 8$ , the structural formula becomes  $(\Sigma\text{R})_{0.67}(\text{Si}_{0.87}\text{Al}_{0.13})\text{O}_{2.75} \cdot 2.6\text{H}_2\text{O}$ , where  $(\Sigma\text{R})_{0.67} = \frac{1}{8}(\text{Ti}_{0.04}\text{Fe}^{3+}_{2.62}\text{Fe}^{2+}_{0.60}\text{Mn}_{0.01}\text{Mg}_{1.58}\text{Ca}_{0.15}\text{Na}_{0.26}\text{K}_{0.07})$ , and again the Ca, Na, K, and 0.25 of the Mg cations are exchangeable. This formula is very similar to that listed in Table 2 with the same  $-1.14$  negative charges per unit cell without the assumption of a 2:1 layer structure. With this formula, the entire weight loss is accounted for by the  $\text{H}_2\text{O}$  content (no hydroxyl ions).

The weight loss at high temperatures (Figure 1) may be due to  $\text{H}_2\text{O}$  molecules in the small pores (Van der Marel and Beutelspacher, 1976) and less accessible (probably) inner spheres. The unit-cell charge of  $-1.14$  corresponds to a CEC of about 135 meq/100 g, which is much larger than the 60 meq/100 g. The discrepancy may arise either because the proposed structural formula does not represent the natural configuration of atoms in the material (e.g., not all of Al atoms are in the tetrahedral positions), or because the method used does not extract all of the exchangeable cations. Using a 0.1 M  $\text{LaCl}_3$  solution at pH 7.7 as an extractant (Sameshima and Way, 1982), the amounts of exchangeable Na, K, Ca and Mg were 10.3, 0.77, 0.74 and 62.7, respectively, with a sum of 74.5 meq/100 g, which is still much less than that from the structural formula.

The large negative charge and extensive surface area of the Geelong material, and its much more developed structure compared to the Broken Hill hisingerite-neotocite material (as seen by TEM) suggest that although the Geelong material probably had a gel-like structure initially, it now has some form of layer-structure, as evidenced by the extensive exfoliation of the spherical bodies.

The mode of occurrence and the properties of the Geelong hisingerite-material suggest that it precipitated from hydrothermal solutions at the later stages of cooling. Its composition suggests that it was probably derived from iron-rich glass and/or ferromagnesian silicates. Although such material persists in the joints of the grey basalt, smectite has been found in similar joints of the deeper, more hydrothermally altered green basalt, possibly replacing what could have been hisingerite material. Removal of iron from the structure in some laboratory-induced hydrothermal reactions (to be reported later) yielded hematite and a swelling smectite with sharp basal reflections. TEM shows the resulting particles to be regular sheets of smectite, indicating that the smectite in the joints of the lower green basalt layer could have been produced by the hydrothermal reactions of such material.

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**Резюме**—Материал, похожий на описанный в литературе гизингерит, находился в соединениях кайнозойского серого базальта в близости Гилонг в Виктории. Материал дает порошковую дифрактограмму со слабыми широкими линиями при 4,49, 2,58, и 1,53 Å, а химический анализ материала следующий: SiO<sub>2</sub> = 34,2; TiO<sub>2</sub> = 0,28; Al<sub>2</sub>O<sub>3</sub> = 4,16; Fe<sub>2</sub>O<sub>3</sub> = 17,10; FeO = 3,52; MnO = 0,04; MgO = 5,19; CaO = 0,68; Na<sub>2</sub>O = 0,26; P<sub>2</sub>O<sub>5</sub> = 0,05; H<sub>2</sub>O+ = 5,3; H<sub>2</sub>O– = 25,4; сумма = 96,18% (3,82% включения сидерита). Принимая модель смектита с 44 отрицательными зарядами на элементарную ячейку, химический состав дает формулу для элементарной ячейки с –1,14 зарядами, соответствующую катионообменной способности (КОС) равной 135 мэкв/100 г. Такой же самый заряд элементарной ячейки получается, когда структурная формула рассчитывается на основании (Si + Al) = 8. Измеренная величина КОС, равная 60 мэкв/100 г, указывает на то, что структура смектита не относится к этому гизингеритовому материалу и что в альтернативной структуре все атомы Al не могут находиться в тетраэдрических местах. Хотя удельная площадь поверхности этого материала находится между 662 и 758 м<sup>2</sup>/г (сравнимая с величиной для смектита), инфракрасные спектры не показывают полос характеристических для OH, и кривые по термальному анализу не имеют пика дегидроксилирования при 550–600°C, ожидаемого для смектита. Трансмиссионная электронная микроскопия показывает симптомы слоистой структуры и видимые пустые сферические тела с луковичной структурой и внутренним диаметром 140 до 200 Å, которые могут представлять местонахождения больших количеств воды, содержащейся в этом материале. Вид залегания и характер гизингеритового материала указывают на его осаждение из раствора при относительно низкой температуре. [E.G.]

**Resümee**—Eine Substanz, die der entspricht, die in der Literatur als Hisingerit beschrieben wurde, wurde in den Spalten des känozoischen grauen Basalts in der Nähe von Geelong, Victoria, gefunden. Das Material ergibt ein Röntgenpulverdiffraktogramm mit schwachen, breiten Linien bei 4,49, 2,58, und 1,53 Å und eine chemische Analyse mit SiO<sub>2</sub> = 34,2; TiO<sub>2</sub> = 0,28; Al<sub>2</sub>O<sub>3</sub> = 4,16; Fe<sub>2</sub>O<sub>3</sub> = 17,10; FeO = 3,52; MnO = 0,04; MgO = 5,19; CaO = 0,68; Na<sub>2</sub>O = 0,26; P<sub>2</sub>O<sub>5</sub> = 0,05; H<sub>2</sub>O+ = 5,3; H<sub>2</sub>O– = 25,4; Summe = 96,18% (3,82% Siderit-Verunreinigung). Legt man ein Smektitmodell mit 44 negativen Ladungen pro Elementarzelle zugrunde, so ergibt die chemische Zusammensetzung eine Formel für die Elementarzelle mit –1,14 Ladungen, was einer Kationenaustauschkapazität (CEC) von 135 meq/100 g entspricht. Die gleiche Ladung der Elementarzelle erhält man, wenn man die Strukturformel auf der Basis Si + Al = 8 berechnet. Der gemessene CEC-Wert von 60 meq/100 g deutet darauf hin, daß die Smektitstruktur auf dieses Hisingerit-Material nicht angewendet werden kann, und daß in einer Alternativstruktur nicht alle Al-Atome Tetraederplätze besetzen. Obwohl die spezifische Oberfläche dieses Materials zwischen 662 und 758 m<sup>2</sup>/g beträgt (was vergleichbar mit der von Smektit ist), zeigt das Infrarotspektrum keine charakteristischen (OH)-Schwingungen, und die Kurven der thermischen Analyse haben keinen Dehydroxilierungsspeak bei 550°–600°C, den man bei einem Smektit erwartet. Transmissionselektronenmikroskopische Untersuchungen zeigen Hinweise für eine Schichtstruktur und offensichtlich hohle kugelige Körper mit einer "Zwiebelschalenstruktur" mit einem inneren Durchmesser von 140–200 Å. Dies könnten die Plätze sein, auf denen der hohe Wassergehalt dieses Materials sitzt. Die Art, wie dieses Hisingerit-Material vorkommt, und seine Eigenschaften deuten auf eine Entstehung durch Ausfällung aus einer Lösung bei relativ niedrigen Temperaturen hin. [U.W.]

**Résumé**—Un matériau semblable à ce qui a été décrit dans la littérature comme étant de l'hisingerite a été identifié dans les joints de basalte gris Cénozoïque près de Geelong, Victoria. Le matériau donne un cliché de diffraction de rayons-X avec de faibles larges sommets à 4,49, 2,58, et 1,53 Å, et une analyse chimique de  $\text{SiO}_2 = 34,2$ ,  $\text{TiO}_2 = 0,28$ ,  $\text{Al}_2\text{O}_3 = 4,16$ ,  $\text{Fe}_2\text{O}_3 = 17,10$ ,  $\text{FeO} = 3,52$ ,  $\text{MnO} = 0,04$ ,  $\text{MgO} = 5,19$ ,  $\text{CaO} = 0,68$ ,  $\text{Na}_2\text{O} = 0,26$ ,  $\text{P}_2\text{O}_5 = 0,05$ ,  $\text{H}_2\text{O}^+ = 5,3$ ,  $\text{H}_2\text{O}^- = 25,4$ , total = 96,18% (3,82% impureté sidérite). En admettant un modèle smectite avec 44 charges négatives par maille, la composition chimique donne une formule de maille avec  $-1,14$  charges, ce qui correspond à une capacité d'échange de cations (CEC) de 135 meq/100 g. On obtient la même charge de maille lorsque la formule structurale est calculée sur la base de  $(\text{Si} + \text{Al}) = 8$ . La CEC de 60 meq/100 g mesurée indique que la structure de la smectite ne peut être appliquée à ce matériau-hisingerite, et que dans la structure alternative, tous les atomes Al ne sont peut-être pas dans les positions tétraédrales. Quoique l'aire de surface spécifique de ce matériau est entre 662 et 758  $\text{m}^2/\text{g}$  (comparable à celle de la smectite), les spectres infrarouges ne montrent pas les vibrations OH caractéristiques, et il manque aux courbes d'analyse thermique le sommet de déshydroxylation à 550–660°C comme l'on s'attendrait d'une smectite. La microscopie d'électrons à transmission montre des indications d'une structure à couches, et des corps sphériques apparemment creux avec une structure "onion" de 140 à 200 Å de diamètre interne, qui pourraient représenter les sites de larges quantités d'eau contenues dans le matériau. Le mode d'occurrence et la nature du matériau-hisingerite suggère la précipitation à partir d'une solution à des températures relativement basses. [D.J.]