

HYDROTHERMAL RHYOLITIC ALTERATION IN THE CASTLE MOUNTAINS, CALIFORNIA

by

HENDRIK HEYSTEK*

International Pipe and Ceramics Corp.

ABSTRACT

X-ray diffraction, differential thermal, chemical analysis and cation exchange data indicate a progressive genesis upon hydrothermal alteration of rhyolitic materials in an extensive fault zone. Kaolinite, a Ca-Mg beidellite, mixed-layer beidellite-hydrous mica and beidellite-vermiculite clay minerals, quartz, cristobalite and feldspar commonly occur in the deposit.

Detailed studies show that the sequence of the 2 : 1 clay mineral alteration is beidellite-hydrous mica mixed-layer \rightarrow beidellite-vermiculite mixed-layer \rightarrow beidellite. This mineralogical change parallels a progressive decrease in the layer charge and amount of fixed K^+ present and an increase in exchangeable Ca^+ and Mg^+ respectively.

INTRODUCTION

Since the early 1920's, white-burning ceramic clay has been mined from deposits in an area of the southwest slope of the Castle Mountains near the old Hart Townsite and twelve miles east of Ivanpah. Here flow-layered Tertiary rhyolites and associated tuffs and breccias contain extensive zones of hydrothermal alteration along steeply dipping to vertical fractures (Cleveland, 1957, p. 140). The rhyolites strike northward and dip 15° to 30° westward.

The alteration zones (along lines of post volcanic faulting) range from a few feet to several hundred feet wide and probably as much as 1000 ft long. Although the zones are clay-rich, they also contain residua of partly altered to relatively fresh rhyolite which in mining and processing are commonly mixed and ground with the clay as part of the commercial material.

The P.S. Hart property (Location: sec. 19, T. 14N., R. 18E., S.B.M.) has been owned and operated by Gladding, McBean & Co. since 1941. In early operations, clay was removed by a series of low angle stopes driven eastward into the hillside, beneath a layer of relatively unaltered rock. Beginning in 1948, opencut benching has been employed and a quarry opened parallel to the hillside. Active mining is confined to a few weeks each year when clay-bearing rock is blasted from the quarry walls and moved to layered stockpiles. This material is ground and used in the Glendale Plant for the production of wall tile.

* 2901 Los Feliz Boulevard, Los Angeles 39, California.

During 1961, 40 drill holes (80–190 ft deep) were sunk at the P.S. Mine (Fig. 1) to obtain data that would enable the Company to evaluate the quality and quantity of the clay reserves. Based on the data obtained from the mineralogical investigation of about one thousand samples, several conclusions on the clay mineralogy and possible genesis of the deposit have been made and are discussed herein.

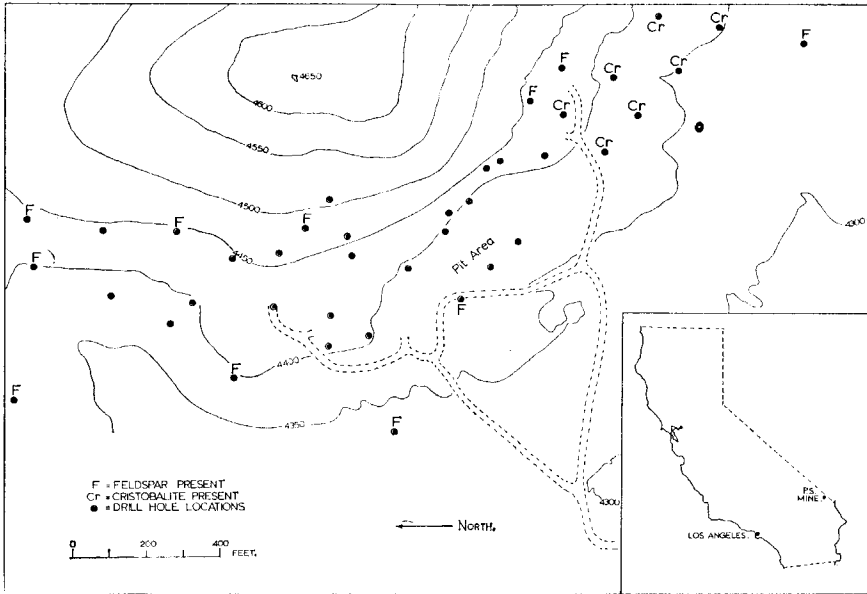


FIGURE 1.—P.S. mine.

MINERALOGY OF THE DEPOSIT

A total of 750 samples were received for mineralogical evaluation (X-ray diffraction and differential thermal analysis) with the individual samples representing 5 ft sections from the drill holes. A further 250 samples were collected at the quarry and from adjacent prospecting trenches. After powder X-ray diffractometer patterns (Norelco unit, CuK_α , 1.5404) were obtained from all the samples, it was possible to group together samples that had similar mineralogical compositions (Fig. 2) for subsequent determination of their ceramic properties.

Two silica minerals (alpha quartz and cristobalite) were present in the samples investigated, as well as feldspar in some cases. The clay minerals occurring in the deposit were kaolinite, beidellite and mixed-layer clay minerals. In Fig. 3 are reproduced X-ray diffractometer records of essentially pure fractions of these materials, obtained by fractional sedimentation of some drill hole samples.

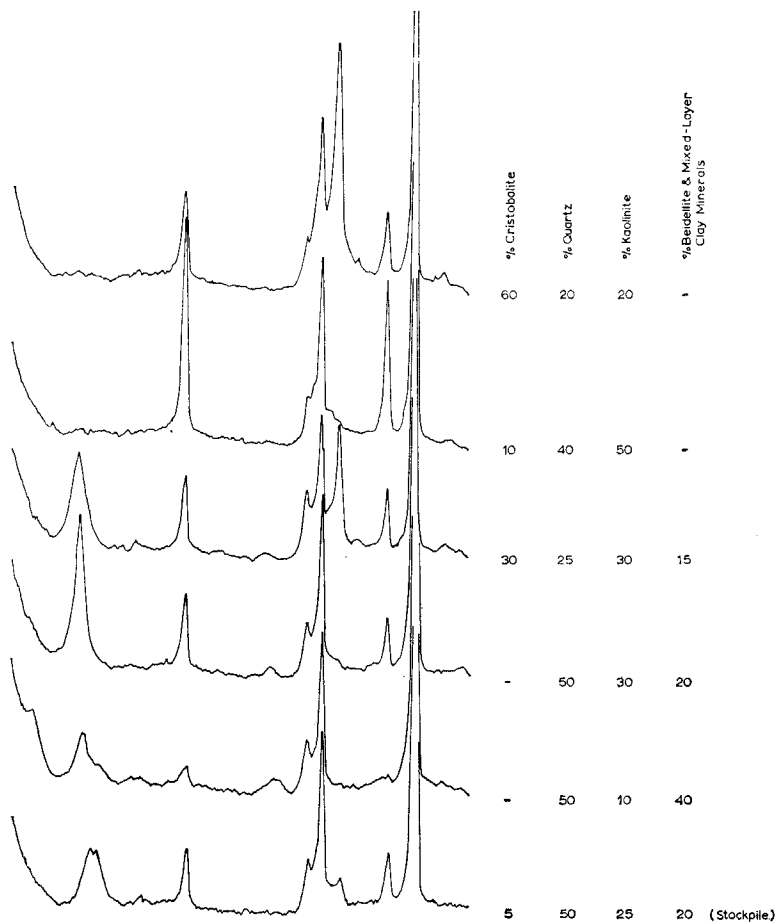


FIGURE 2.—X-ray diffractometer curves of typical mineral combinations occurring in P.S. deposit.

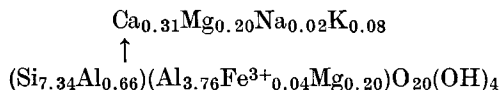


FIGURE 3.—X-ray diffractometer curves of minerals in P.S. clay.

The material mined and then compiled in the stockpiles consists of about 5 per cent cristobalite, 50 per cent quartz, 25 per cent kaolinite and 20 per cent montmorillonite and mixed-layer minerals with the following average chemical analysis:

SiO ₂	73.79%
Al ₂ O ₃	16.52
Fe ₂ O ₃	0.29
TiO ₂	0.10
CaO	1.62
MgO	0.94
K ₂ O	0.53
Na ₂ O	0.08
Loss Ign.	5.87
	99.74%

The montmorillonite occurring in this deposit is a dioctahedral type, closely approaching the idealized beidellite formula (Brown, 1961, p.156–p.190) as shown by the chemical analysis (Table 1, Col. 1) and the formula calculated from it (Mackenzie, 1960, p.2).



This corresponds to a Si:Al ratio of 3.3:2 and a mineral with the structural charge located mainly in the tetrahedral layers. Furthermore, a Li-saturated sample after being heated to 200–300°C overnight “expanded” upon glycolation, a test suggested by Greene Kelley (1953) to identify beidellite.

Using the ammonium acetate Kjeldahl distillation method of cation exchange determination, a total cation exchange capacity of 100 meq per 100 g clay dried at 110°C was found. The ammonium acetate leach liquor was also analysed and found to contain Ca⁺⁺ (60 meq) and Mg⁺⁺ (35 meq) totalling 95 meq per 100 g clay. This corresponds to all the Ca⁺⁺ and one-half of the Mg⁺⁺ of the naturally occurring clay, confirming the value from Kjeldahl distillation.

In addition to this beidellite, some closely related interstratified clay minerals appeared in other parts of the deposit that may be generally grouped as:

- (1) a beidellite–hydrous mica mixed-layer mineral,
- (2) a beidellite–vermiculite mixed-layer mineral, and
- (3) a combination of both these mixed-layer types.

1. The basal X-ray diffraction peaks of the beidellite–hydrous mica mixed-layer clay mineral are reproduced in Fig. 4 and show intense sharp peaks at 12.8 Å and 26.12 Å. Ethylene glycol treatment caused an increase of the 12.8 Å and 26.12 Å values to 13.8 Å and 28.11 Å respectively with a third

TABLE 1.—CHEMICAL ANALYSIS OF "PURE" CLAY MINERAL FRACTIONS

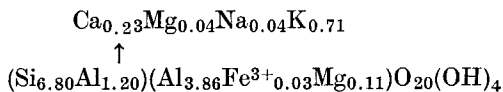
	1	2	3	4
	Beidellite	Beidellite and Beidellite-Vermiculite Mixed-Layer	Beidellite-Vermiculite & Beidellite-Hydrous Mica Mixed-Layer	Beidellite- Hydrous Mica Mixed-Layer
SiO ₂	55.80	52.90	51.50	52.00
Al ₂ O ₃	28.60	32.95	33.00	33.00
Fe ₂ O ₃	0.41	0.09	0.33	0.36
TiO ₂	0.26	—	0.20	0.31
CaO	2.23	1.50	1.01	1.62
MgO	2.03	1.81	1.48	0.74
Na ₂ O	0.09	0.14	0.15	0.17
K ₂ O	0.48	1.04	3.92	4.25
Loss on Ignition	9.70	9.28	8.39	7.85
	99.60	99.71	99.98	100.30

STRUCTURAL FORMULAS BASED ON CHEMICAL ANALYSIS

- (1)
$$\begin{matrix} \text{Ca}_{0.31}\text{Mg}_{0.20}\text{Na}_{0.02}\text{K}_{0.08} \\ \uparrow \\ (\text{Si}_{7.34}\text{Al}_{0.66}) (\text{Al}_{3.76}\text{Fe}^{3+}_{0.04}\text{Mg}_{0.20}) \text{O}_{20} (\text{OH})_4 \end{matrix}$$
- (2)
$$\begin{matrix} \text{Ca}_{0.21}\text{Mg}_{0.25}\text{Na}_{0.03}\text{K}_{0.17} \\ \uparrow \\ (\text{Si}_{6.85}\text{Al}_{1.15}) (\text{Al}_{3.89}\text{Fe}^{3+}_{0.01}\text{Mg}_{0.10}) \text{O}_{20} (\text{OH})_4 \end{matrix}$$
- (3)
$$\begin{matrix} \text{Ca}_{0.14}\text{Mg}_{0.18}\text{Na}_{0.03}\text{K}_{0.66} \\ \uparrow \\ (\text{Si}_{6.76}\text{Al}_{1.24}) (\text{Al}_{3.86}\text{Fe}^{3+}_{0.03}\text{Mg}_{0.11}) \text{O}_{20} (\text{OH})_4 \end{matrix}$$
- (4)
$$\begin{matrix} \text{Ca}_{0.23}\text{Mg}_{0.04}\text{Na}_{0.04}\text{K}_{0.71} \\ \uparrow \\ (\text{Si}_{6.80}\text{Al}_{1.20}) (\text{Al}_{3.86}\text{Fe}^{3+}_{0.03}\text{Mg}_{0.11}) \text{O}_{20} (\text{OH})_4 \end{matrix}$$
 Beidellite-Hydrous
Mica Mixed-Layer
- $$\begin{matrix} \text{Ca}_{0.14}\text{Na}_{0.06}\text{K}_{1.33} \\ \uparrow \\ (\text{Si}_{6.26}\text{Al}_{1.74}) \text{Al}_{3.98}\text{Fe}^{3+}_{0.02} \text{O}_{20} (\text{OH})_4 \end{matrix}$$
 Formula of the Hydrous
Mica in Mixed-Layer

order reflection represented at 9.22 Å. Upon heating to 450°C only one peak at 10.11 Å occurs, indicating the interstratification of a montmorillonitic and hydrous mica clay minerals in a nearly regular 1:1 stacking arrangement (Heystek, 1954; Brown, 1961, p.428).

These X-ray data are in agreement with a cation exchange value of 60 meq per 100 g clay dried at 110°C and the chemical analysis (Table 1, Col. 4). The following formula was derived from the analysis:



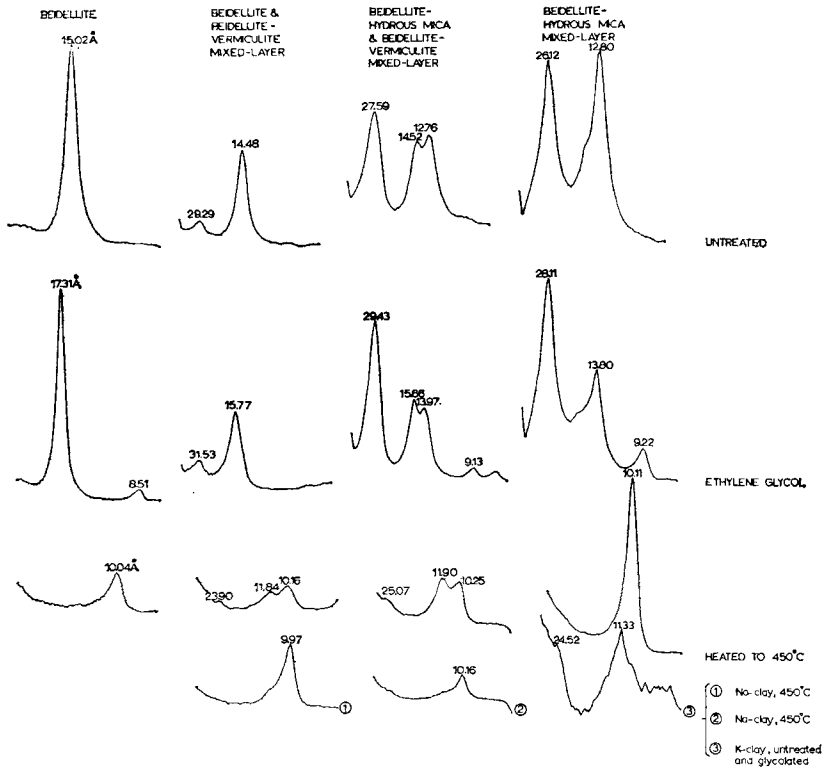
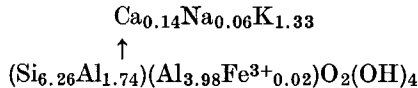


FIGURE 4.—Basal X-ray diffraction peaks of beidellite and mixed-layer clay minerals after various treatments.

If differences in chemical composition occur between the two types of layers, this formula must be regarded as an average. If, however, about 50 per cent of the interstratified material is considered to be similar in composition to the beidellite previously discussed, the hydrous mica constituent will have the following calculated formula:



very similar to the hydromuscovite described by Brammell, Leech and Bannister (1937). A K-saturated sample of this beidellite-hydrous mica mixed-layer clay mineral showed basal diffraction peaks at 11.33 Å and 24.52 Å (Fig. 4) and also after being saturated with ethylene glycol (Weaver, 1953). Repeated drying (110°C) and wetting of the K-saturated sample resulted in a material that had a single basal reflection of 10.1 Å.

2. Another mixed-layer clay mineral combination that occurred in the deposit appeared to be nearly regular 1:1 interstratification of beidellite and vermiculite layers; there was, however, always some beidellite as such present in the clay mineral fractions of this mixed-layer combination. The basal reflections (Fig. 4) at 14.48 Å and 29.29 Å increased to 15.77 Å and 31.55 Å upon glycolation and decreased to 11.84 Å and 23.9 Å respectively, upon being heated to 450°C. A reasonably regular repetition of 14.5 Å and 17.3 Å layers after glycolation is indicated by the values of 15.77 Å and 31.55 Å. When an Na-saturated sample was prepared and heated to 450°C, only one peak at 9.97 Å appeared.

The observed differences of the X-ray diffraction results upon various treatments of this "clay vermiculite" compared to the beidellite appear to be due only to the type and distribution of the naturally occurring interlayer cations and slight differences in layer charge (Brown, 1961, pp.180, 314 and 318).

This would be substantiated by the behavior of the Na-treated material and a comparison of the chemical analyses reported in Table 1 which indicate a progressive change in the layer charge with less replacement of Si^{4+} by Al^{3+} in the tetrahedral layer; some replacement of Al^{3+} by Mg^{2+} in the octahedral layer, and less fixed K^+ present. The term "vermiculite" is used for the interlayered clay mineral that in this case presented X-ray diffraction data, after various treatments, similar to that of the macroscopic mineral vermiculite.

3. Another characteristic mixed-layer clay mineral grouping that occurred commonly in this deposit was a combination of beidellite-hydrous mica and beidellite-vermiculite mixed layers; i.e. a combination of the interstratified minerals discussed above, under 1 and 2. The basal X-ray diffraction peaks of this material are reproduced in Fig. 4 and the chemical analysis reported in Table 1, Col. 3.

The cristobalite that occurs in certain parts of the deposit (Fig. 1) is of interest because, although sharp X-ray diffraction peaks were evident (Fig. 3) for this material, the endothermic peak at 250°C on the differential thermal analysis curve (Mackenzie, 1957, p.291) was much less intense than for synthetically prepared cristobalites—about 1/25 as intense. Infrared curves obtained on this naturally occurring cristobalite, amorphous silica and synthetically prepared cristobalites indicate that the cristobalite in this deposit has a very poorly ordered structure (paper being prepared for publication).

GENESIS OF THE DEPOSIT

At the P.S. Mine (Fig. 1) the hydrothermal alteration zone (about 300 ft wide and 2000 ft long) followed a fault striking NW-SE. The limits of the alteration are indicated by rhyolitic material containing increasing amounts of unaltered feldspar. The most intense alteration appears to be in the south-eastern part of the deposit, with progressively less altered areas occurring

towards the northwest as suggested by the sequence of the mineralogical distribution in the deposit.

In the southeastern part of the deposit, cristobalite, quartz and kaolinite predominate, with some beidellite also present. In the pit area very little, if any, cristobalite occurs, and quartz with the clay minerals kaolinite, and beidellite predominates. Proceeding in a northerly direction, a gradual decrease in the amount of the beidellite clay mineral and increasing association with first a beidellite-vermiculite and then a beidellite-hydrous mica interstratification is apparent. Mixed-layer clay mineral assemblages have been frequently reported as commonly occurring in hydrothermal alteration deposits (Grim, 1953; Bundy and Murray, 1959; Tooker, 1955).

An evaluation of the mineralogical composition of the thousand or more samples collected at the deposit, as well as of 50 complete chemical analyses (some are recorded in Table 2) indicates that the deposit generally shows a

TABLE 2.—CHEMICAL ANALYSIS OF MATERIAL TYPICAL OF ALTERATION ZONES IN P.S. DEPOSIT

	Material Typical of Alteration Zones in P.S. Deposit (Fig. 1)				
	Wall-rock	North-western Areas		Main Pit	So. Eastern
SiO ₂	76.81	75.98	75.02	74.70	76.70
Al ₂ O ₃	11.46	14.62	15.02	15.99	15.63
Fe ₂ O ₃	1.32	0.80	0.56	0.33	0.45
TiO ₂	0.14	0.12	0.10	0.12	0.10
CaO	1.14	1.00	1.20	1.04	0.46
MgO	0.16	0.43	1.08	0.80	0.19
Na ₂ O	1.03	0.29	0.38	0.04	
K ₂ O	5.05	2.64	1.28	0.63	0.38
Loss On Ignition	1.71	3.85	4.87	5.92	5.88
Total	98.82	99.73	99.51	99.57	99.79
Predominant Minerals	Quartz Feldspar	Beidellite- Hydrous Mica Mixed-Layer	Beidellite & Beidellite- Vermiculate Mixed-Layer	Beidellite Kaolinite	Cristobalite Kaolinite

trend of horizontal variations. Much less or no differences were noticeable in material occurring at different depths (80–190 ft) in any particular locality. This suggests that the parent material in the alteration zone did not have a variable mineralogical or chemical composition and was most likely originally similar to the unbrecciated, and therefore less permeable, slightly altered fringe area rock (Table 2). The chemical analyses of the altered material do show a progressive decrease in per cent K₂O, though, and an increase in

Al_2O_3 and combined H_2O . This chemical change is more apparent when the chemical analyses of the 2:1 clay minerals occurring in the different zones are compared (Table 1).

The clay mineral alteration sequence appear to be first a beidellite-hydrous mica mixed-layer mineral, followed by a beidellite-vermiculite mixed-layer mineral, and proceeding through beidellite to kaolinite. Among the samples investigated, it was possible to find these minerals occurring together in all possible ratios but always indicating the mineralogical trend suggested above. The progressive change of hydrous-mica to vermiculite to beidellite requires only slight changes in layer charge due to lattice substitutions with a subsequent decrease in fixed interlayer K^+ , Ca^{2+} and Mg^{2+} interlayer cations that replace the K^+ allow the mineral to show "swelling" characteristics.

CONCLUSIONS

Hydrothermally altered Tertiary rhyolites show a generalized alteration sequence of clay minerals as follows: (1) beidellite-hydrous mica mixed-layer (nearly a 1:1 regular interstratification); (2) beidellite-vermiculite mixed-layer; (3) a Ca-Mg beidellite and (4) kaolinite.

The montmorillonite occurring in this deposit is classified as a beidellite because of a Si:Al ratio of 3.3:2. Although interstratified vermiculite behaves like the macroscopic mineral vermiculite upon X-ray diffraction after various treatments, its chemical composition is not similar. This seems to be true for many of the "clay vermiculites" reported in the literature.

Differences in layer charge caused essentially by substitution of Al^{3+} for Si^{4+} in the octahedral layers and the presence of various amounts of different interlayer cations explain the common occurrence of mixed-layer clay minerals in this deposit. Examples of all stages of progressive alteration from beidellite-hydrous mica through beidellite-vermiculite interstratifications were found among the samples (clay mineral fractions) investigated.

REFERENCES

- Brammell, A., Leech, J. G. C. and Bannister, F. A. (1937) The paragenesis of cookeite and hydromuscovite associated with gold at Ogofau, Carmarthenshire: *Min. Mag.*, v.24, pp.507-519.
- Brown, G. (1961)(ed.) *The X-Ray Identification and Crystal Structures of Clay Minerals*: Mineralogical Society, London, 544pp.
- Bundy, W. M. and Murray, H. H. (1959) Argillization in the Cochiti mining district, New Mexico: in *Clays and Clay Minerals*, 6th Conf., Pergamon Press, pp.342-368.
- Cleveland, G. B. (1957) Clay: *Mineral Commodities of California*, California Division of Mines, Bull. 176, pp.131-152.
- Greene-Kelly, R. (1953) The identification of montmorillonoids in clays: *Jour. Soil Science*, v.4, pp.233-237.
- Grim, R. E. (1953) *Clay Mineralogy*: McGraw-Hill Inc. N.Y., pp.323-330.
- Heystek, H. (1954) An occurrence of a regular mixed-layer clay-mineral: *Min. Mag.*, v.30, pp.400-408.

168 ELEVENTH NATIONAL CONFERENCE ON CLAYS AND CLAY MINERALS

- Mackenzie, R. C. (1960) The evaluation of clay mineral composition with particular reference to smectites: *Silicates Industriels*, pp.12-18 and 71-75.
- Mackenzie, R. C. (1957) (ed.) *The Differential Thermal Investigation of Clays*: Mineralogical Society, London, 456pp.
- Tooker, E. W. (1955) Altered wall rocks along vein deposits in the central city—Idaho Springs region, Colorado: in *Clays and Clay Minerals*, Natl. Acad. Sci.-Natl. Res. Council, pub. 456, pp.348-361.
- Weaver, C. E. (1953) Mineralogy and petrology of some Ordovician K-bentonites and related limestones: *Geol. Soc. Amer. Bull.*, v.64, pp.921-944.